









# Index to Volume XXVIII, 1906.

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## BORIC ACID: ITS DETECTION AND DETERMINATION IN LARGE OR SMALL AMOUNTS.

BY WILSON H. LOW.

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MANY good articles have been published on the detection and determination of boric acid, but they are rather fragmentary in character, and while helping in one direction, have left much to be desired in another. Most processes are tedious of execution and do not give evidence that all the boric acid will be obtained.

I have discovered two points in regard to the detection and determination of boric acid, which I believe are new.

One of these is that in the qualitative test it is not necessary to dry the turmeric paper at the temperature of the water-bath, but that the test carried on at the ordinary temperature in the air or vacuum desiccator, or even at 40–50° in a desiccator, is exceedingly delicate and allows the detection of boric acid in the presence of large amounts of other salts and in the presence of such interfering agents as nitrates and phosphates, when it would be entirely overlooked by the ordinary methods.

I do not know the limit of the qualitative test, but such small quantities of boric acid as 0.000001 gram in 1 cc. or 0.0000001 gram in 0.10 cc. are easily recognized, and these same quantities would undoubtedly be recognized by the evaporation of larger quantities of the solvent.

The other point applies to the quantitative determination. It is very difficult to distil off all the boric acid from an aqueous solution, by passing the vapor of methyl alcohol through it. As

long as any quantity of water remains it will retain boric acid, but it has been found that, by adding some substance to unite with the water, it is possible to distil off the total boric acid easily and with no tedious evaporation to dryness, with the attendant bumping and danger of breakage. Such a substance is the dry, granulated, chemically pure calcium chloride.

The methods described below have been in use about three years, and a great many experiments have been made to test the various points brought out. Further experiments will bring out other points of value, but the methods are in good shape and if followed as directed, will give the desired result. The methods will first be given as they are expected to be carried out, and further on will be given the experiments, or some of them, on which the processes stand. The action of indicators in the presence of boric acid and in the presence of methyl alcohol will also be given.

Wherever methyl alcohol is mentioned, the laboratory refined Columbian or Colonial spirits of commerce is meant. In the refined state, as it is purchased, it contains boric acid and this has to be removed and the alcohol tested to make sure it is entirely free from it.

#### QUALITATIVE TEST.

The test is given as applied to meat products, but obviously it may be applied to anything where the boric acid can be obtained in a soluble form. Ten grams of the hashed meat are placed in a metal dish (the cover of a three-pound lard pail is as good as anything, if well cleaned) and moistened with 5 cc. of a  $N/2$  solution of sodium carbonate or its equivalent. Place on the steam-bath or in an oven till about dry. Drying may be done nicely on a small electric stove. Ignite the dry mass, over a burner that heats the whole bottom of the dish evenly. Do not use a high heat. Thoroughly carbonize the ash, but do not bother to burn off much of it. Burning off is dangerous, as boron compounds may be volatilized when ignited in the presence of carbon. Direct experiments have shown this. The carbonized ash is placed in a mortar (a glass mortar is best) and ground up somewhat and then about 10 cc. of water containing 1 cc. of strong hydrochloric acid added and triturated with it. Filter off through a small filter (a small Witt's plate is best, as it retains very little

liquid) into a flat platinum or glass dish. A Petri dish 7-10 cm. in diameter is good.

About 1 cc. or less of the solution is taken and placed in a watch-glass and evaporated on the steam-bath with a piece of turmeric paper. If boric acid is present in the food product as a preservative, and there are no interfering agents, such as nitre, present, then a test for boric acid will be obtained here. This does not mean that if a test is obtained here the food product necessarily contained boric acid added for preserving purposes, but merely that the test is delicate enough to detect any possible amount of boric acid that would be added intentionally. The main lot of solution is placed in a shallow dish with a piece of turmeric paper, and then placed in a desiccator till *perfectly* dry. A vacuum drying oven is best, as the drying is rapid. I use a vacuum drying oven and can control the heat, using generally 40-50° and about 700 mm. vacuum. The smallest traces of boric acid will show up in this test. It is more delicate, if anything, if the drying is done in an ordinary desiccator, but the time of drying is very long. Tests that fail utterly on the steam-bath will show up strongly under these conditions. Nothing which I have tried, such as nitre, salt, sulphates or even phosphoric acid, has interfered with the test. Nitre will destroy the test carried on on the steam-bath and many other salts will seriously interfere. Make sure the turmeric paper is perfectly dry, for incrusting salts often give the appearance of dryness while the underlying paper is still moist. Food products should not be condemned because a strong test is obtained by operating in this manner. Added boric acid is easily detected by moistening the turmeric paper with the solution and drying on the steam-bath. If nitre is present, it can be gotten rid of (for the steam-bath test) by igniting with sufficient organic matter or, better, by distilling off the boric acid with methyl alcohol and testing the distillate. In testing qualitatively, the best result seems to be given with a solution containing at least one-tenth its volume of free strong hydrochloric acid, if the test is made on the steam-bath. For the test at ordinary temperature or at 40-50° a slight excess of acid is all that is needed, though greater excess does no harm. For the delicate test I should advise against the use of the trade mark glasses, as they are borosilicates and I have some indications that they will give up boric acid. •

In the following tests the final volume before evaporation was 2 cc. unless otherwise stated. The turmeric paper was about  $50 \times 9$  mm. and the ordinary paper supplied by chemical dealers. A steam-bath was used with the first twenty tests.

The last test repeated on the steam-bath will bleach the paper owing to the formation of chlorine compounds.

Many other tests have been tried and nothing found to interfere with the test made by drying in the vacuum desiccator or oven.

There appears to be no loss of boric acid in concentrating a large volume of solution in the vacuum, and the test is just as strong as where only 1 cc. is used. 0.00001 gram of boric acid is equivalent to 0.0001 per cent. when 10 grams of material are operated on, and this quantity is infinitesimal for a preservative. As far as that is concerned, the simplest kind of a test, carried out in the roughest manner, is amply delicate to detect any boric acid added for preserving purposes. The exception to be noted is where there is a nitrate present.

#### QUANTITATIVE TEST

*Reagents.*—Methyl alcohol free from boric acid; methyl orange indicator; *p*-nitrophenol indicator; phenolphthalein indicator; hydrochloric acid free from boric acid; calcium chloride, granulated, chemically pure; standard solution of sodium hydroxide, as free as possible from carbonate; standard solution of sulphuric acid, as free as possible from carbonate; whether these solutions are normal or of other strength depends on what quantity of boric acid is being dealt with. Both normal and tenth-normal are useful.

*Standard Solutions.*—The standard solutions of acid and alkali are made up in this laboratory from distilled water which has been distilled from a block-tin (solid) still and condenser and subsequently boiled hard for about twenty minutes in another block-tin vessel furnished with a connection to a large soda-lime column. After boiling, the vessel is furnished with a tin condensing pipe inside to cool the water rapidly. All air entering the vessel has to come through the soda-lime column, and the water keeps free from carbonic acid. While 100 cc. of the ordinary distilled water will take about 15 drops of N/10 sodium hydroxide solution to give a *permanent* coloration with phenolphthalein, the boiled water allows the permanent coloration to show up

Test.	Final volume of solution, cc.	Boric acid present, Gram	Excess of strong HCl	Other things present.	Indications
1	2.00	0.000000	2 drops	Nothing	None
2	2.00	0.000010	2 drops	"	Merest trace
3	2.00	0.0000100	2 drops	"	Strong test
4	2.00	0.000050	2 drops	"	Slight test
5	2.00	0.000025	2 drops	1 cc. N/1 NaOH	None
6	2.00	none added	2 drops	1 cc. N/1 NaOH	None
7	2.00	0.000025	2 drops	1 cc. N/1 NaOH	Slight trace
8	2.00	0.000050	4 drops	1 cc. N/1 NaOH	Merest trace
9	2.00	0.0000100	4 drops	1 cc. N/1 NaOH	Merest trace

The above tests show the sensitiveness without interfering substances present and also how sodium chloride interferes, when present.

10	2.00	0.000050	2 drops	5 cc. Ba(OH) <sub>2</sub>	No test
11	2.00	0.0000100	4 drops	1 cc. N/1 NaOH	Merest trace
12	2.00	0.0000100	2 drops	Salt from 1 cc. N/1 NaOH	Merest trace
13	2.00	0.0000150	2 drops	Nothing	Good test
14	2.00	none added	2 drops	Salt from 1 cc. N/1 NaOH	Trace
15	2.00	0.0000100	10 drops	Salt from 1 cc. N/1 NaOH	Slight trace
16	2.00	0.0000200	2 drops	Salt from 1 cc. N/1 NaOH	Slight trace
17	2.00	0.0000200	10 drops	Salt from 1 cc. N/1 NaOH	Slight test
18	2.00	0.0000250	2 drops	Salt from 1 cc. N/1 NaOH	Slight test
19	2.00	0.0000300	2 drops	Salt from 1 cc. N/1 NaOH	Plain test
20	2.00	0.0000100	2 drops	15 gms. of sand + 2 cc. of curcuma solution	Faint test

The following tests were made at the ordinary temperature or not to exceed 40° C. Either a vacuum drier or an ordinary desiccator was used. V = vacuum drier and D = desiccator.

21 V	2.00	0.0000100	2 drops	Salt from 1 cc. N/1 NaOH	Strong test
22 V	2.00	0.000010	2 drops	Salt from 1 cc. N/1 NaOH	Plain test
23 D	1.00	0.0000010	1 drop	Nothing	Strong test
24 D	0.10	0.0000001	1 drop	Nothing	Plain test
25 V	10.00	0.0000100	1 drop	1 cc. saturated sol. Na <sub>2</sub> CO <sub>3</sub>	Strong test
26 V	10.00	0.0000100	1 drop	1 drop of syrupy phosphoric acid	Strong test
27 V	10.00	0.0000100	1 drop	1 cc. potassium nitrate solution	Strong test



strongly with one drop, and this is almost sufficient for a litre of the boiled water. Incidentally, I will remark that sodium thiosulphate solutions made up with this water will keep their correct strength almost indefinitely and deposit no sulphur.

*Preparation of the Methyl Alcohol.*—"Columbian" or "Colonial Spirits" are introduced into a still of some kind and made *strongly* alkaline with some very concentrated caustic soda or potash. If a glass vessel is used, it must be furnished with a capillary boiling tube, and the size of this tube adapted to the size of the flask, etc.<sup>1</sup> Distil off the alcohol carefully and run a blank through the apparatus (putting alkali in the boiling flask) and see if there is any titratable amount of boric acid given off. If not, the alcohol is all right. Where the alcohol is to be used to collect the boric acid for a subsequent qualitative test, it must be purified till 100 cc. of distillate give no test for boric acid qualitatively.

*Effect of Methyl Alcohol on p-Nitrophenol and on Phenolphthalein.*—The alcohol recently distilled from an excess of alkali is meant in all cases. 100 cc. of the alcohol were taken and one drop of the nitrophenol indicator added. The color was yellow. N/10 sulphuric acid was run in till the solution was colorless. 0.90 cc. was used. One drop of N/1 sodium hydroxide brought back the yellow very strong. Experiment repeated except N/1 sulphuric acid was used. Result the same, two drops = 0.10 cc. being used. This relationship between one drop of nitrophenol and methyl alcohol holds roughly for various dilutions and a delicate method of testing for acidity in methyl alcohol might be arranged from this fact. In our case all we wanted was to make sure that we could titrate the mineral acid in the methyl alcohol distillate fairly close, and this is demonstrated.

Phenolphthalein is of little use in titrating acidity in methyl alcohol. Great dilution is necessary before the indications are good. But after the alcohol is made neutral or slightly alkaline (after previously being acid) to nitrophenol then phenolphthalein may be depended on to indicate pretty closely the end-point for a boric acid titration.

*Indicators.*—Phenolphthalein is made up by dissolving 5 grams in 500 cc. of ethyl alcohol and making up to 1 liter. Use about 1 cc. in tests.

<sup>1</sup> See Heyward Scudder: This Journal, 25, 163.

*p*-Nitrophenol.—This indicator was ordered as nitrosophenol and came marked as nitrosophenol, but as it fails to give Liebermann's reaction for nitroso compounds and has a melting-point of about  $113^{\circ}$  it must be simply *p*-nitrophenol and not the nitroso-compound.

Make up by dissolving 1 gram in 75 cc. of neutral ethyl alcohol and add 25 cc. of water. Use 1 drop to 100 cc. of the solution to be titrated. As this indicator is, perhaps, not well-known I will give its properties as I have found them. My attention was first called to this indicator by an article by L. Spiegel in the *J. Chem. Ind.* **19**, 1049 (1900). He recommends it to replace methyl orange. I can corroborate his statements and also those he makes in the same journal **23**, 682, where he takes issue with Lunge on its being able to replace methyl orange for many titrations. This indicator is about as sensitive as phenolphthalein. Colorless with mineral acids and intensely yellow with caustic or carbonated alkalis. With bicarbonates the yellow shade is much weaker, but still bicarbonates can be titrated, if care is used. In boric acid titrations, avoid carbonates as much as possible. If 100 cc. of water is made just alkaline to nitrophenol, on adding glycerol the solution becomes colorless when boric acid is present, though boric acid gives no indication in aqueous solution, unless it is a strong solution, in which case even methyl orange will react acid. No distinct end-point can be obtained with nitrophenol in the presence of glycerol and boric acid. As the boric acid comes nearer to  $\text{NaBO}_2$  the color of the solution becomes more intensely yellow, and this acts as a guide to the phenolphthalein end-point.

*Methyl Orange* —One gram dissolved to 1 liter in water. It may be used in place of nitrophenol in aqueous solution, but not in methyl alcohol. It has the advantage over nitrophenol of being less sensitive to carbonic acid (though it is by no means entirely indifferent to this acid) and also less sensitive to boric acid in a strong aqueous solution. Its disadvantages are that it is not nearly as sensitive as nitrophenol and the end-reactions run through several shades of color, and it cannot be used in methyl alcohol with any accuracy. I seldom use it for boric acid titrations.

We have found that methyl orange and nitrophenol give the same end-points in titrating sodium hydroxide or ammonia.

Remember always that the color is much weaker in the presence of bicarbonates.

In the absence of interfering agents and complete absence of carbonic acid, phenolphthalein, methyl orange and nitrophenol in aqueous solution will give identical end-points.

#### QUANTITATIVE TEST.

The limit of the test, as here arranged, is 1 drop or 0.05 cc. of N/10 sodium hydroxide solution. This corresponds to 0.00031 gram of boric acid or 0.00062 per cent. or about 0.10 ounce per 100 pounds of the food product, a quantity absurdly small for any preservative effect.

The sample of meat or other food product is ground up or hashed and 50 grams of the well-mixed sample taken and placed in a clean cover of a three-pound lard pail, or other similar dish. Spread the meat in a layer over the dish and moisten with 25 cc. of N/1 sodium carbonate solution or equivalent, and dry on the steam-bath, oven or electric stove. It is a great advantage to dry before igniting, as by so doing the meat does not swell up, and burns off much easier. The quantity of sodium carbonate directed to be added is more than sufficient to retain 1 per cent. of boric acid, and this is more than would be used. 25 cc. of N/2 sodium carbonate are generally sufficient and makes the burning to carbonaceous ash quicker. Ignite gently, heating the whole bottom of the dish, if possible, to a carbonaceous ash free from brown products soluble in water. Do not burn off all the carbon. Allow to cool and with a spatula scrape out the ash into a smooth mortar (a glass mortar is best). Grind up fairly fine and transfer from the mortar to the distillation flask. This is easily done as the smooth mortar allows the ash to slide out completely. Put about 10 cc. of water into the dish from which the ash was scraped, add 1 cc. of strong hydrochloric acid and allow to act about thirty seconds (we want to avoid dissolving the iron to any extent) and then pour into the distillation flask. This will sufficiently wash out the dish, and there would be no particular loss if this step was left out. About 3 to 5 cc. of strong hydrochloric acid are added to the distillation flask and the ash allowed to soak in the liquid for a few minutes to dissolve as much as possible, the object being to get all the boric acid in solution. Ten to 15 grams of dry, granulated, chemically pure calcium chloride are now added and allowed to dissolve as much as will in a few minutes.

shaking. Connect up the flask in its place in the distillation system and pass methyl alcohol vapor through. Usually no attempt is made to heat this flask except by the methyl alcohol vapor itself, but there is no harm in so doing after 50 to 100 cc. of the alcohol have condensed in it. When about 100 cc. of distillate has been obtained, it is drawn off and tested. The distillation is allowed to go on without interruption and each 100 cc. or less are drawn off and tested till no more boric acid is found. When the last distillate gives a test requiring only 1 drop of N/10 sodium hydroxide solution the process is generally assumed finished, as without great care the blank test on the glycerol alone or in the presence of salts will vary a drop. If necessary, the determination can be made absolutely to within 1 drop of N/10 sodium hydroxide.

Each distillate is tested as follows: It is drawn off into a flask similar to the distillation flask (a round-bottomed flask holding up to the neck about 275 cc.) and 1 drop of nitrophenol indicator solution added. N/1 sodium hydroxide solution is dropped in till the yellow color of the indicator is seen. Practically all the mineral acid that has distilled over is now neutralized. Experiment shows that very little mineral acid does distil over, even with a large excess in the distillation flask, unless the contents of the distillation flask are concentrated. Now add about 1 cc. of the phenolphthalein indicator and run in N/1 sodium hydroxide solution till the pink color is seen. As soon as you are sure the coloration is reddish or pink, that will do without making it strong. The difference between the end-points with nitrophenol and phenolphthalein will be a close measure of the boric acid present, as the methyl alcohol takes the part of glycerol and would probably be just as good as the latter but for its peculiar effect on some indicators. After finding how many cubic centimeters correspond to the boric acid, add twice as much more alkali; that is, if the difference in end-points between nitrophenol and phenolphthalein was 10 cc. then add 20 cc. more of the alkali. This is to insure enough alkali to combine with the boric acid to form  $\text{Na}_3\text{BO}_3$ , which is certainly enough to prevent loss of boric acid on evaporating off the methyl alcohol. In all probability, this is more than enough. The compound or mixture of boric acid and alkali that is stable in boiling methyl alcohol is stated by E. Polenske<sup>1</sup> to have the composition  $5\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ , and this is

<sup>1</sup> J. Chem. Ind., 20, 273 (1901).

apparently a mixture of  $\text{NaBO}_2$  and  $\text{Na}_2\text{O}$ . Now put a capillary boiling tube into the flask and evaporate off the methyl alcohol on the steam-bath. When the alcohol has evaporated, dissolve the residue in about 25 cc. of water, and run in N/1 sulphuric acid till the solution is colorless. If a large quantity of N/1 sodium hydroxide solution has been used, necessitating a large quantity of acid, it is better to drop in strong hydrochloric acid till the solution is colorless, thus keeping the bulk down. Next, holding the neck of the flask with a clamp, put the flask into the steam-bath for a few minutes, take out and quickly connect with the suction pump (a large-sized Chapman is very good). The flask will be rapidly exhausted and the solution will boil vigorously and all carbon dioxide will be expelled. The evaporation cools the contents of the flask rapidly and, if there is any doubt that all carbon dioxide has been expelled, the heating and boiling may be repeated, as there is no fear of losing boric acid, except mechanically. Note that the solution should be colorless when hot as well as when cold; if not, add more acid and heat again. Sometimes the yellow color of the nitrophenol is seen in the hot liquid, due to the decomposition of the bicarbonates and showing that not enough acid has been added. The phenolphthalein indicator will often separate out as an insoluble white precipitate as the solution cools. This is of no particular consequence as it clears up again later, and experiments seem to indicate that 1 cc. of this indicator solution is better to use than a smaller quantity. The solution is now cold and free from carbon dioxide. Break the vacuum and run in N/1 sodium hydroxide solution till the last drop turns the nitrophenol indicator yellow. Now run back to acid reaction with 1 drop of N/1 sulphuric acid, and then run to just alkaline reaction with N/10 sodium hydroxide. In some cases in running to alkaline reaction with N/10 sodium hydroxide solution, the yellow color is very faint (due to large amounts of salts present or possibly to carbon dioxide not previously expelled), but usually it is well marked. At any rate run to the first point that you are sure is yellowish. Now take 40 cc. of strong glycerol in the 50 cc. graduated cylinder and pour it into the flask, rotating the latter to mix the contents. About 35 cc. of glycerol will flow out with moderate draining. The titration with N/10 or N/1-sodium hydroxide solution (depending on how large a quantity of boric acid is present, and the titration in methyl

alcohol has indicated this) is proceeded with till the last drop gives a decided color change to a reddish or pinkish shade. It is not necessary to run to a decided pink color as one drop of N/10 sodium hydroxide solution in excess makes a decided change from the strong yellow of the nitrophenol to a color with a reddish tint due to phenolphthalein. The progress of the titration is well seen in the change of depth of color due to nitrophenol. As the end-point is approached, the yellow color grows very intense. The difference between the end-point to nitrophenol and phenolphthalein multiplied by 0.0062024 gives the grams of boric acid, if N/10 alkali has been used in the titration. Each 100 cc. of distillate, or whatever quantity is drawn off each time, is tested in this way. A blank had best be run by taking 10 cc. of N/1 sodium hydroxide solution, adding a slight excess of N/1 sulphuric acid and about 10 cc. of water and boiling under vacuum as in the test, and then bringing to just alkaline reaction to nitrophenol with N/10 sodium hydroxide solution, adding the same amount of glycerol and titrating to the end-point with phenolphthalein indicator.

There need be no mistaking the end-points, and test experiments have shown that nitrophenol gives the same end-point as methyl orange (first noticeable change), and is greatly to be preferred, as there is no change through several shades to the end, as there is with methyl orange. However, methyl orange may be used with equal accuracy, paying due attention to running to the same shade of end-point each time. An exception must be made to the last statement in regard to the preliminary titration of the boric acid when in methyl alcohol solution. Methyl orange here is of no value. If for any reason it is found necessary to use more than 10 cc. of water and 5 cc. of hydrochloric acid in the distillation flask, it will be necessary to increase the amount of calcium chloride to take care of the additional water. Use about two-thirds of a gram of calcium chloride to 1 cc. of the aqueous solution in the distillation flask. The idea is to have all the boric acid in solution as then it is quickly volatilized. The arrangement of the apparatus will be seen from the sketch.

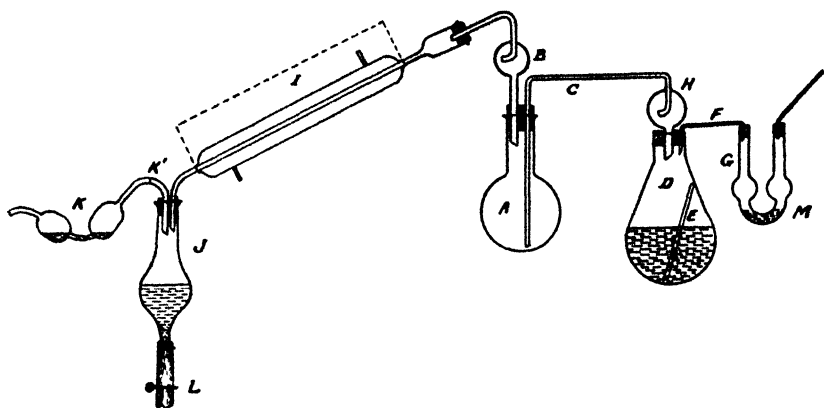


Fig. 1

- A, distillation flask. Capacity about 275 cc. Rests in asbestos cloth on retort stand ring.
- B, splash trap, about 5 cm. in diameter. From top of flask to top of bend is about 12 cm.
- C, vapor tube. Internal diameter about 4 mm. and at end inside the flask  $2\frac{1}{2}$  mm. this tube must not have too small an opening in the flask on account of danger of becoming clogged.
- D, flask made from an 800 cc. Jena glass Kjeldahl digestion flask, cut off as shown. The methyl alcohol is boiled in this flask. It is furnished with the absolutely necessary boiling tube E.
- E, boiling tube about 16 cm. long with a capillary bore. About 1 cm. from the end in the alcohol it is sealed. Without this tube the alcohol on boiling bumps fearfully and would endanger the apparatus and operator. With this tube the boiling is easy, uniform and without danger. It is necessary to shake out the alcohol from the capillary and put it back into the alcohol, each time the solution is started boiling.
- F, bend and rubber tube connecting the boiling flask with the small safety U-tube.
- G, U-tube of small size containing a little mercury in the bend. This acts as a safety-valve in case the apparatus gets clogged, and prevents the blowing out of the stopper from the boiling flask. A long tube leads from the U-tube to carry off the alcohol vapor should it blow out. The rubber tube should slope towards the boiling flask.
- H is a splash trap the same as B, except that the tube leads from it at right angles. It is connected with C, by a sliding piece of rubber tubing.
- I is the condenser about 38 cm. long between the dotted lines and about 50 cm. over all.
- J is the collecting flask. Mine is made by blowing out the bottom of a 200 cc. Erlenmeyer flask and drawing down to a tube. It is furnished with a rubber tube and pinch-cock at the bottom.

K is the absorption tube with the water seal, to prevent loss of methyl borate. At the end of each 100 cc. of distillate, the contents of this tube are run into the distillate taken off. K' = rubber connection.

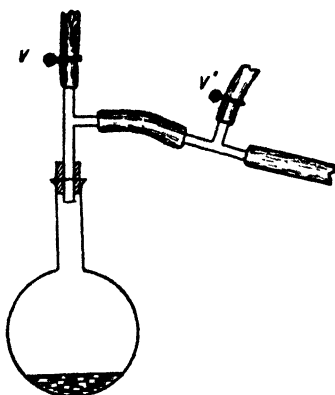


Fig. 2.

Flask connected to vacuum pump VV' are T tubes and rubber tubing with screw pinch-cocks. The vacuum should always be broken by opening cock V, to prevent any possible return of condensed water.

The following results are from an actual test: Fifty grams of meat taken + 25 cc. N/2 sodium carbonate solution.

First distillate, about 100 cc. After making alkaline to nitrophenol, took about 590 cc. N/1 sodium hydroxide to phenolphthalein end-point. Enough to make in all 177 cc of the N/1 sodium hydroxide were added. After evaporating off the alcohol and getting the residue in proper solution, the titration for boric acid took 4 cc. of N/1 sodium hydroxide + 21.7 cc. N/10 sodium hydroxide, equivalent to 61.70 cc. N/10 solution in all. Deduct 0.25 cc. for the glycerol blank leaves 61.45 cc. as due to the boric acid in the first 100 cc. of distillate.

The boiling and distillation flasks are set on asbestos cloth and held in retort rings and clamps.

The apparatus works perfectly and I cannot say too much about the absolute necessity of the boiling tube at every stage where methyl alcohol is boiled in glass. In a metal dish it will boil without bumping, but not in glass. The boiling flask has some phenolphthalein added to it and enough concentrated sodium hydroxide (practically carbonate-free) to keep it permanently red. This insures no boric acid in the vapor.

All stoppers are of cork.



Second distillate, about 100 cc., took 6 cc. N/10 sodium hydroxide for the boric acid. This minus 0.25 for the glycerol blank leaves 5.75 cc. for the boric acid. The preliminary titration in methyl alcohol solution had indicated about 5.50 cc.

Third distillate, about 100 cc., took 0.57 cc. N/10 sodium hydroxide and this minus 0.25 cc. for the glycerol blank leaves 0.32 cc. for the boric acid.

Fourth distillate, about 50 cc., took 0.25 cc. N/10 sodium hydroxide, and this is the quantity taken by the glycerol alone, so all the boric acid has been obtained.

Total N/10 sodium hydroxide used for boric acid = 67.52 cc. and this multiplied by 0.0062 = 0.4168 gram = 0.837 per cent. on the meat taken.

This is a large quantity to be present under the circumstances and was more than I expected. Had it not been for the preliminary titration in methyl alcohol solution, enough alkali to retain the boric acid might not have been added and loss would have occurred while evaporating off the methyl alcohol. Had more calcium chloride been added at the start the first two distillates would probably have contained all the boric acid.

*Action of Boric Acid on Some Indicators.*—In all the following experiments, unless otherwise stated, the water used was free from carbon dioxide.

A solution of more than 2 grams of boric acid in 100 cc. will react acid to methyl orange and also to nitrophenol, more so to the latter than the former. Direct experiments have shown, however, that nitrophenol gives perfectly accurate results in boric acid titration, if carried out as directed. It is a great advantage to expel all carbon dioxide, and this applies to methyl orange as well.

*Loss of Boric Acid on Ignition with Organic Matter.*—On igniting boric acid and meat, strongly, to burn off as much carbon as possible, greenish flames were seen and the ash when tested gave a very slight qualitative test for boric acid, while there had been enough originally present to give a strong test.

Numerous experiments have been made to test the process at every essential point. Instead of giving the experiments in detail it will, perhaps, be sufficient to give in direct statements the results.

(1) A solution containing a small amount of boric acid may be concentrated from 100 cc. to 10 cc. without fear of a titratable amount of boric acid being lost.

(2) Boiling a dilute solution of boric acid to free it from carbon dioxide occasions no loss, unless the boiling is prolonged.

(3) All carbon dioxide is expelled from distilled water by heating to boiling and then applying vacuum for a few minutes till the solution is almost cold.

(4) Starting with a mixture in the distillation flask of 25 cc. of water and 25 cc. of methyl alcohol and passing methyl alcohol vapor through the mixture, while keeping the latter approximately at the same volume, it took fifty-five minutes and over 400 cc. of distillate before the temperature of the vapor leaving the distillation flask was anywhere near the boiling-point of methyl alcohol, showing the difficulty of driving off the water.

(5) Ten cc. of boric acid solution containing 0.3125 gram and 40 cc. methyl alcohol were distilled with methyl alcohol vapor. Seven successive distillates failed to get over all the boric acid.

(6) Where a water trap was not used the boric acid recovered was, in a certain case, equivalent to 4.90 cc. N/1 sodium hydroxide. Where a water trap was used 5.05 cc. N/1 sodium hydroxide were required. Theory called for 5.04 cc.

(7) By distilling a mixture of 1 volume of aqueous solution of boric acid with 10 volumes of methyl alcohol, till only 3 cc. of the mixture were left, about four-fifths of the boric acid were found in the distillate and one-fifth left in the flask.

(8) It was found that if calcium chloride was added to the distillation flask in the proportion of about 0.5 gram for each cubic centimeter of solution, all the boric acid came over quickly and completely. Using two-thirds of a gram of calcium chloride is better yet, unless some conditions make it impracticable to use this amount.

#### NOTES.

Make sure the methyl alcohol and calcium chloride used give no distillate containing a titratable quantity of boric acid. This may be insured by placing the calcium chloride in a separate flask, connecting with the distillation apparatus, acidifying with several drops of hydrochloric acid and passing methyl alcohol vapor through till the distillate gives no titration for boric acid.

This solution of calcium chloride is then added to the test instead of the solid salt. Nickel dishes or deep crucibles are very good for evaporating off alkaline solutions of methyl alcohol, containing boric acid. No boiling tube is required. While our method of freeing the solution from carbon dioxide, by boiling under a vacuum after heating on the steam-bath, appears all that could be desired, it is not suitable for freeing a solution of calcium bicarbonate from excess of carbon dioxide. Actual boiling under atmospheric pressure is required in this case as direct experiments have shown.

Sometimes iron appears to distil over with the methyl alcohol, when the contents of the distillation flask are strongly acid. This causes the end-point with nitrophenol to be somewhat obscure, as the solution will take on a reddish tinge before the strong yellow due to excess of alkali. It makes the solution look as if the phenolphthalein end-point was about to be reached, before the nitrophenol end-point had been seen. This has only occurred a few times and did little harm. This was noticed so recently, that I have not proved it to be caused by iron, but it appears to be iron.

In conclusion, I would like to draw attention to the very wide distribution of boric acid. It occurs in almost everything we meet in the food line, and caution should be used in reporting food as containing boric acid as a preservative without a quantitative determination. Ten grams of food product are quickly burned to ash and 50 to 100 cc. of methyl alcohol distilled from this ash will contain most of the boric acid, or even all, unless it is present in some quantity. Now 1 drop of  $N/10$  sodium hydroxide on this quantity will equal 0.0031 per cent. of boric acid, much too small a quantity to have been added for preserving purposes, and yet large enough to have given a strong qualitative test.

Boric acid occurs naturally in apples and probably in other fruits and vegetables. It is present in almost all common salt and some kinds contain relatively considerable amounts of it.

Below will be given some results on salts used in packing-house products. The results are rather under than over the truth, as some of the tests were made without all the necessary refinements of the process as it now stands.

Designation of the salt.	Boric acid. Per cent.	Grains per pound avoird.
Kansas No. 2 rock salt.....	0.005000	0.35
Foreign sea salt.....	0.010900	0.76
Foreign sea salt.....	0.006448	0.45
Cheshire salt .....	0.000992	0.07
XXX Casing salt.....	0.000620	0.0435
Kansas fine salt.....	0.000620	0.0435
Kansas rock salt No. 2.....	0.001240	0.0870
Louisiana rock salt .....	0.000992	0.06944

There is not a salt here but what would give a good qualitative test by the delicate method indicated in this paper, and some of them would show up under the less refined test of the steam-bath.

THE CUDAHY PACKING CO.,  
SOUTH OMAHA, NEB

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[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

## AVAILABILITY OF PHOSPHORIC ACID OF THE SOIL.<sup>1</sup>

BY G. S. FRAPS.

Received May 4, 1906

THE availability of the constituents of a soil depends upon several factors. The chemical compounds which are capable of being absorbed by plants and are exposed to the action of the plant roots may be termed *chemically available*. The compounds enclosed in the soil grains, or otherwise protected from soil moisture or the action of plant roots, may be called *physically unavailable*. During the growing season of the plant, chemically or physically unavailable food is converted into chemically available forms. This may be termed *weathering availability*. Further, different plants have different powers of utilizing the plant food presented to them; this may be termed a *physiological availability*. All these factors are worthy of consideration in soil problems. Chemically available plant food has been given the greatest attention, but for success in solving the problems of the soil all factors must be considered and valued.

In seeking a method for the determination of chemically available phosphoric acid, several factors again must be considered: first, the solubility of the soil phosphates in the solvent; second, the solubility of other soil constituents; third, fixation by the soil; and fourth, availability of the chemically available plant food.

<sup>1</sup> Read at the New Orleans meeting of the American Chemical Society.

*Solubility of Phosphatic Minerals.*—Phosphates of calcium, aluminum, and iron, the latter more or less basic, and the mineral apatite, are perhaps the most common phosphates in the soil, though vivianite, phosphorite, and, less often, phosphatic minerals, such as dufrenite, wavellite, triplite, and others may be present. These phosphates differ in the readiness with which they yield their phosphoric acid to plant roots, and, if possible, the solvent used for determining chemically available phosphoric acid should make some difference between them.

Dr. F. W. Clarke, Chief Chemist of the Geological Survey, considers that apatite makes up 99 per cent. of the phosphoric acid of igneous rocks. Vivianite is quite common in secondary clays as a mineral. Of course, in the soil, other secondary minerals are quite likely to occur, particularly in soils in which a portion of the phosphates have passed through plants.

The author determined the solubility of some mineral and precipitated phosphates in a few solvents, under the conditions of soil analysis. The method used was as follows:

The amount of material containing 0.2 gram phosphoric acid (equivalent to 100 grams soil containing 0.2 per cent. phosphoric acid) was brought in contact with 1000 cc. solvent, and maintained at 40° for five hours. It was then filtered, and phosphoric acid determined in 100 cc. of the filtrate by the volumetric method. The results are presented in Table I.

TABLE I.—PERCENTAGE OF PHOSPHORIC ACID PRESENTED DISSOLVED BY DIFFERENT SOLVENTS.

	N/200 HCl.	N/50 HCl.	N/5 HCl.	N/5HNO <sub>3</sub> .	1 Per cent. citric acid.
Aluminum phosphate precipitated .....	46.25	100	100	100	100
Calcium phosphate precipitated.....	100	100	100	100	100
Ferric phosphate precipitated .....	8.5	16.0	100	100	100
Phosphorite (Ca).....	48.3	85	100	100	71
Wavellite (Al) .....	1.8	3.6	5.6	3.6	2.2
Vivianite (Fe).....	28.0	36.0	100	97.8	94.8
Triplite (Fe, Mn) .....	16.8	41.2	98.8	99.5	25
Dufrenite (Fe).....	0.8	2.0	4.0	1.5	2.0
Apatite (Ca).....	15.8	47.0	100	100	25.5

Fifth-normal hydrochloric and nitric acids dissolve completely the precipitated phosphates of aluminum, calcium, and iron, and phosphorite, triplite, vivianite, and apatite. Wavellite and dufrenite are attacked only slightly.

One per cent. citric acid entirely dissolves the precipitated phosphates; it has only one-fourth the power of the mineral acids for apatite and triplite. It dissolves less vivianite and much less phosphorite than the mineral acids.

The high solubility of vivianite and triplite in the weak solvents is striking. According to these experiments, fifth-normal hydrochloric or nitric acid should dissolve from a soil containing 0.2 per cent. phosphoric acid, all the phosphorite, apatite, vivianite, triplite, and precipitated phosphates of calcium, aluminum and iron, with which the solvent comes in direct contact. These compounds are undoubtedly of different value to plants, but these acids make no distinction between them.

Fiftieth-normal hydrochloric acid has a greater solvent power than 1 per cent. citric acid for phosphorite, triplite and apatite, but not for vivianite or ferric phosphate. N/200 hydrochloric acid, as was to be expected, has the lowest solvent power.

As soils contain much less than 0.2 per cent. phosphoric acid soluble in N/5 mineral acids, and since decreasing the amount of phosphoric acid presented to the solvent should increase the *percentage* dissolved, the soil phosphates may have a higher solubility in N/50 and N/200 acid, or citric acid, than is indicated by the work just given. On the other hand, in these experiments the minerals were presented in fine powder, and all sides came in contact with the solvent. In a soil, part of the phosphatic material may be in the soil particles, so that only one side is exposed to the solvent.

*Solubility of Other Soil Constituents.*—The plant food in the soil is in part protected from plant roots and soil moisture by surrounding material, such as hydrated oxide of iron, carbonate of lime, mica, feldspar, etc. If any of these are dissolved, physically unavailable plant food is exposed to the solvent, and dissolves to a greater or less extent. It is impossible to select a solvent which does not have some action of this kind, and all practicable solvents dissolve the carbonates of lime and magnesia if present. For this reason the direct comparison of calcareous and siliceous soils does not appear allowable. If, for example, a calcareous and a siliceous soil expose the same amount of phosphoric acid to plant roots, on treatment with acid the calcareous soil would give up more phosphoric acid, as the carbonates, on dissolving, would expose an additional quantity of phosphates to the action of the

solvent. The soil with the larger quantity of material soluble in the solvent used, would show a larger quantity of chemically available phosphoric acid than it really contains.

It might be necessary to divide soils into different classes, according to the amount of material soluble in the solvent used for determining available plant food.

The different amounts of phosphoric acid dissolved from the same soil by different solvents, must be due, in part at least, to their different powers of dissolving the silicates, oxide of iron, or other soil constituents which protect the phosphates.

*Fixation by Soil Constituents.*—If a solvent loses phosphoric acid to the soil, it is evident that it cannot be considered as reliable for determining the chemically available plant food. With such a solvent the solution obtained does not represent the solubility of the soil constituents, but contains the quantity dissolved less the quantity fixed. This consideration eliminates certain solvents, such as water, carbonated water, and acetic acid.

With *water* the phosphoric acid in solution represents a condition of equilibrium between the solubility of the soil phosphates and the fixing power of the soil. For example, the author<sup>1</sup> brought eight soils in contact with water and with a solution of potassium phosphate containing 4 parts of phosphoric anhydride per million. At the end of twenty-four hours, 3.1 and 2.5 parts per million, respectively, were present. Thus nearly the same result is obtained whether we start with water, or a solution of potassium phosphate. F. H. King<sup>2</sup> observed a great absorption in three minutes.

The aqueous soil extract does not represent the solubility of the soil phosphates in water; neither does it represent the strength of solution with which the roots come in contact. The solvent power of the water near the roots is increased by the carbon dioxide they excrete, and dissolved food may be taken up by the plant without ever coming in contact with fixing soil particles, and thereby having its strength reduced.

*Carbonated water*, according to P. Wagner,<sup>3</sup> loses phosphoric acid rapidly to carbonate of lime and hydrated ferric oxide, and a soil extract with carbonated water lost phosphoric acid in contact with the soil.

<sup>1</sup> Bulletin 82, page 16, Texas Experiment Station (1906).

<sup>2</sup> Investigations on Soil Management, p. 159.

<sup>3</sup> J. Landw., 1871, 89.

Dilute *acetic* acid, according to Wagner and Gerlach,<sup>1</sup> behaves similarly to carbonated water.

*Citric acid*.—With 2 per cent. citric acid, König<sup>2</sup> recovered 73 to 84 per cent. of the phosphoric acid fixed by four soils. He also added different amounts of water-soluble phosphoric acid to soil and recovered all of it with the citric acid.

*Experiments with Nitric Acid*.—Solutions of N/50 nitric acid containing 0.2 gram phosphoric acid per liter were brought in contact with a number of materials, five hours at 40°. No absorption occurred with prehenite, siderite, hematite, or limonite. With 0.5 gram precipitated aluminum hydroxide per liter, 12.5 per cent. of the phosphoric acid was absorbed, and with ferric hydroxide, 25.5 per cent. Fixation during the treatment of a soil with this solvent thus appears possible; and still more probable with N/200 acid.

*Availability of Phosphoric Acid in the Soil*.—The most soluble phosphates placed in the soil are never completely removed by a single crop, so we cannot expect the natural phosphates of lime, etc., in the soil to have a high availability or approach 100 per cent. In other words, the chemically available phosphoric acid should be considerably more than is taken up by a single crop.

The writer made experiments on four soils of similar character, to determine the availability of chemically available phosphoric acid, assuming that the plant takes all its phosphoric acid from compounds soluble in N/5 nitric acid. These results are only comparative. In determining the availability of phosphatic fertilizers, the quantity of phosphoric acid recovered is not taken as the availability of the material, but is compared with one of the fertilizers taken as a standard. The same should hold good in the determination of the availability of the phosphoric acid in the soil, though a standard is difficult to decide upon. Tricalcium phosphate in pure sand might be used.

The experiments were carried out as follows:

Twelve and one-half pounds of each soil were placed in galvanized iron pots, which had previously received a layer of gravel. Each pot received 2 grams sodium nitrate, 5 grams calcium carbonate, and, after the plants had made some growth, 1 gram ammonium nitrate. In addition, one pot received 1.5 grams potassium sulphate containing 0.82 gram  $K_2O$ , a second 2.5 grams

<sup>1</sup> Landw. Verss., 1905, 371.

<sup>2</sup> Ibid., 46, 201 (1896).



acid phosphate, containing 0.35 gram available phosphoric acid, and a third both potassium sulphate and phosphoric acid. Twelve cowpeas weighing 2.00 grams were planted in each pot on May 31st, came up June 2nd, and grew until August 4th, when the experiment was discontinued on account of red spiders. All leaves that fell off were saved. The pots were watered two or three times a week, weighing them from time to time to maintain an equal water content between the pots (40 to 80 per cent. of their water capacity).

At the end of the period, analysis was made of the plant, roots and seed, and phosphoric acid determined in the soil by N/5 nitric acid. The results are summarized in Table II.

TABLE II.—AVAILABILITY OF PHOSPHORIC ACID.

	Soil 174. Gram.	Soil 176. Gram.	Soil 178. Gram.	Soil 180. Gram.
Phosphoric acid in plant.....	0.0440	0.0302	0.0439	0.0340
Phosphoric acid in seed. ....	0.0198	0.0198	0.0198	0.0198
Difference ....	0.0242	0.0104	0.0241	0.0142
In roots.....	0.0220	0.0136	0.0047	0.0060
Total from soil.....	0.0462	0.0240	0.0288	0.0202
	Per cent.	Per cent.	Per cent.	Per cent.
Soluble in N/5 HNO <sub>3</sub> in soil...	0.00235	0.00075	0.0028	0.0010
	Gram.	Gram.	Gram.	Gram.
In each pot.....	0.1333	0.0397	0.1587	0.0567
	Per cent.	Per cent.	Per cent.	Per cent.
Comparative availability (entire plant) .....	35	60	17	28
Comparative availability (roots excluded).....	18	26	15	23

The percentage of phosphoric acid soluble in N/5 nitric acid removed by the plants varies widely when the entire plant is considered; this is in part due to the difficulty in securing the roots from the soil, only a part of the roots being obtained from soils 178 and 180. When only the part of the plant above the surface is considered, the differences are less. The availability is greatest in the soil which contains the least chemically available phosphoric acid.

The high percentage of phosphoric acid soluble in N/5 nitric acid removed from these soils by cowpeas—particularly soil 176—leads one to question whether this solvent is not too weak. We could hardly expect 35 to 60 per cent. of the chemically available phosphoric acid to be absorbed by the plant.

*Relation of Chemically Available Phosphoric Acid to Soil Deficiencies.*—The amount of chemically available phosphoric acid present was compared with the soil deficiency as measured by pot tests with the cowpeas, with the striking result that the order of deficiency was found to be the order of chemically available plant food, and inverse order of the availability of the phosphoric acid.

TABLE III.—AVAILABILITY AND SOIL DEFICIENCY.

Soil.	Phosphoric acid.		Weight of crop. (Dry matter.)	
	In soil. Per cent.	Availability. (Roots excluded.)	With nitrogen and potash.	Phosphoric acid, nitrogen and potash.
176	0.0008	26	14.4	20.7
180	0.0010	23	15.7	20.1
174	0.0024	18	17.0	19.6
178	0.0028	15	20.9	20.1

It does not follow that the same results would be obtained in all types of soils, since different phosphates may be present. With 0.0028 per cent.  $P_2O_5$  soluble in N/5 nitric acid, the soil was no longer deficient in phosphoric acid for cowpeas.

*Physiological Availability*—Pot experiments with cotton, corn, rice, and cowpeas similar to those described above were carried on to compare the solvent powers of these plants for phosphoric acid. Only seven pounds of soil were used in this experiment. The rice soil was left saturated with water during the period of growth, while the other soils were treated as described before.

Cotton and cowpeas removed nearly the same quantity of phosphoric acid. Rice had a lower solvent power, and corn much lower. The results of the experiment are presented in Table IV. The soil contained 0.0021 per cent. phosphoric acid soluble in N/5 nitric acid, equal to 0.0666 gram per pot.

TABLE IV.—AVAILABILITY OF PHOSPHORIC ACID TO DIFFERENT PLANTS.

	Rice.	Cotton.	Cowpeas.	Corn.
Grams $P_2O_5$ taken up.....	0.0124	0.0200	0.0181	0.0032
	Per cent.	Per cent.	Per cent.	Per cent.
Relative availability.....	19	30	27	5
Crop produced :				
	Grams.	Grams.	Grams.	Grams.
With nitrogen and potash.....	5.4	5.7	12.4	4.0
With phosphoric acid, nitrogen and potash.....	15.0	13.7	12.7	36.3

It is seen from the size of the crop produced that the soil appears to be deficient in available phosphoric acid for rice, cotton, and

corn, but not for cowpeas. Corn has the lowest solvent power, and phosphoric acid exerts its greatest effect in this plant. Cotton and cowpeas appear to have nearly the same solvent power, and take up nearly the same amounts of phosphoric acid, but the soil is deficient for cotton and not for cowpeas. This must be due to the cotton requiring more phosphoric acid than cowpeas. We must therefore consider not only the solvent power of the plants, but also their needs for the plant food in question.

The experiment just described brings out clearly the fact that the soil may be deficient in phosphoric acid for some crops, and not for others, and further shows that the deficiency is due not only to the different solvent power of plants for mineral phosphates (physiological availability), but also to difference in the amounts of phosphoric acid required for the growth of the plant. These factors have never been sufficiently regarded in studying the action of solvents upon soils, a soil being often considered as deficient or not deficient in phosphoric acid without regard to the crop used for the test.

Further experiments are required before the availability of phosphoric acid in the order given can be considered as true for all soils. Indeed, Gedroiz found varying relations with different soils in comparing several plants.

*Weathering as Affected by Plants.*—Still assuming that N/5 nitric acid dissolves the chemically available phosphoric acid of the soil, we determined the weathering effect of the plants on the soils. Subtract from the phosphoric acid (soluble in N/5 nitric acid) in the soil before planting, that present after the plants are removed, and the difference gives the loss (or gain) to the soil. Add the amount taken up by the plant, and we have the total amount rendered available. The results are given in Table V, expressed in per cent. of the amount originally present in the soil.

The amount of weathering depends upon the nature of the soil, being in these experiments proportionately more when the content of chemically available phosphoric acid is low.

The author<sup>1</sup> has found that moisture effects a slight average increase in the chemically available phosphoric acid (soluble in N/5 nitric acid) in three months. Calcium carbonate causes a decrease, calcium sulphate an increase, and decaying organic matter an increase. The weathering action of plants is very much greater than that of any of the other agencies studied.

<sup>1</sup> Am. Ch. J. 32, 1 (1904).

TABLE V.—WEATHERING BY PLANTS AND AVAILABILITY.

Plant.	Soil.	Percentage increase by weathering. Per cent.	Comparative availability of phosphoric acid. Per cent.
Cowpeas.....	174	36	25
" .....	176	134	26
" .....	178	38	13
" .....	180	58	23
Cotton.....	.....	39	22
Corn .....	.....	24	4
Cowpeas.....	.....	42	19
Rice.....	.....	57	16

Comparing the plants on the same soil, the order of weathering, beginning with the most active, is rice, cowpeas, cotton, corn. Cotton and cowpeas are nearly the same. Rice acts vigorously.

The foregoing discussion is based on the assumption that all the phosphoric acid removed by the plant was soluble in N/5 nitric acid, which may not be entirely true, though no doubt partly true. Aside from this, however, the weathering action of the plant has undoubtedly changed marked quantities of phosphoric acid into chemically available forms, for more phosphoric acid is present as N/5 soluble after than before growing the plants, and a part of the phosphoric acid taken by the plant must have been in this form. Hence the plant has been active to convert a considerable part of the physically unavailable phosphoric acid into chemically available forms. This the plant could do by breaking down the soil particles, thereby exposing more phosphoric acid to the action of the solvent.

The comparative availability of the phosphoric acid has been calculated from the original content of the soil plus that rendered available by weathering. The results are presented in Table V. The comparative availability is high. We would not expect cowpeas to remove 13 to 26 per cent. of the phosphoric acid presented to them in the form of phosphates of calcium, iron or aluminum. Consequently, it would appear that N/5 nitric acid does not extract all of the chemically available phosphoric acid from these soils.

*Pot Tests Compared with Chemical Tests.*—The striking correspondence between the soil deficiencies as shown by the pot experiments with cowpeas and the chemically available phosphoric acid dissolved by N/5 nitric acid described in previous pages of this article led to the determination of phosphoric acid in a number of soils which had been subjected to pot tests. These pot tests

were made at different times, and were only qualitative in scope, not being intended to measure the *extent* of any deficiencies. They are not strictly comparable.

These results are presented in Table VI. In most cases there is a relation between the amount of phosphoric acid, and the deficiency of the soil as measured by the ratio, crop without phosphoric acid divided by crop with phosphoric acid. The chief exception is soil 128.

TABLE VI.—POT TESTS AND PHOSPHORIC ACID SOLUBLE IN N/5.

Soil No.	Plant	Nitric acid.	
		Phosphoric acid Per cent.	Ratio of crop without with $P_2O_5$ . Per cent.
97	Cotton	0.0007	42
108	"	0.0010	48
141	"	0.0018	66
137	"	0.0029	51
135	"	0.0029	84
128	"	0.0045	62
129	"	0.0065	28
131	Corn	0.0014	22
76	"	0.0022	51
176	Cow-peas	0.0008	70
180	"	0.0010	78
174	"	0.0024	86
178	"	0.0028	100
	"	0.0021	97
	Rice	0.0021	36
	Cotton	0.0021	44
	Corn	0.0021	11

Most of these soils are similar in nature. Some, however, are calcareous.

These experiments do not establish any standard for chemically available phosphoric acid in the soil. They do indicate, however, that the determination of chemically available phosphoric acid is of decided importance in soil analysis, and aids in detecting soil deficiencies, if due attention is paid to the nature of the soil, the kind of crop, and any characteristics which might retard or accelerate ordinary weathering of the soil. Extended series of careful pot experiments in a variety of soils, and much careful chemical work will be necessary before these relations are worked out in detail. Neglect of the other factors which should be considered may lead us astray, and cause us to condemn methods which might give valuable practical information.

## SUMMARY.

(1) The factors to be considered in choosing a solvent for the chemically available phosphoric acid in the soil are (1) solubility of soil phosphates therein; (2) solubility of the soil constituents; (3) fixation by the soil; (4) availability of the chemically available food.

(2) Aluminum, calcium, and ferric phosphates, phosphorite, vivianite, triplite and apatite are completely soluble in N/5 hydrochloric and nitric acids under soil conditions. Some are completely soluble and others less soluble in N/50 HCl, N/200 HCl, and 1 per cent. citric acid.

(3) Other soil constituents, if dissolved, expose physically unavailable phosphoric acid to the action of the solvent, which thereby appears as chemically available. Calcareous soils must thus be placed in a different class from siliceous soils. It is necessary to group soils according to the amount of soluble matter they give to the solvent used for estimating available plant food.

(4) Where fixation takes place, the phosphoric acid in solution represents that dissolved less than fixed. The soil fixes phosphoric acid from water solutions, carbonated water, and acetic acid. Aluminum and ferric hydroxides fix phosphoric acid from N/50 nitric acid under the conditions of soil treatment, and it is possible that some phosphoric acid is removed by the soil from solution when this solvent is used.

(5) Since the soil phosphates are largely insoluble mineral phosphates, they cannot have a high availability; that is, the phosphoric acid extracted by the solvent must be considerably in excess of that consumed by the plant.

(6) Assuming that N/5 nitric acid is a correct measure of chemically available phosphoric acid, its availability was compared in four soils by means of pot experiments as follows: 35, 60, 17, 28 per cent. for the entire plant; 18, 26, 15, 23 per cent. for the aerial portion only.

(7) In the four experiments, the order of availability as measured by pot tests is the same as the order of chemically available plant food as measured by N/5 nitric acid.

(8) Physiological availability was compared in rice, cotton, corn and cowpeas. Corn had the lowest assimilative power, rice next, and cotton and cowpeas nearly equal; the soil was deficient

in phosphoric acid for rice, cotton and corn, but not for cowpeas. While cotton and cowpeas have the same solvent power, cotton needs more phosphoric acid in its growth.

(9) The sum of the phosphoric acid in the soil after growing the plants plus that in the plant, less the original content of the soil, is taken as the phosphoric acid made available by the plant. It varies from 24 to 136 per cent. of the original soil content in our eight experiments, thus varying widely according to the soil or the plant. No doubt, different soils are different in this respect.

(10) In experiments with 15 soils, there appeared to be a relation between the chemically available phosphoric acid as measured by N/5 nitric acid, and soil deficiencies as shown by pot tests.

(11) There is no doubt that the determination of chemically available plant food will give valuable indications as to the needs of soils in phosphoric acid, if due attention is paid to the factors which influence it, and to the other factors of availability.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE. PUBLISHED BY PERMISSION OF THE SECRETARY OF AGRICULTURE. SENT BY H. W. WILEY.]

## HIGH VACUA IN THE SCHEIBLER TYPE OF DESICCATOR.

BY H. C. GORE.

Received April 28, 1906.

THE ether-sulphuric acid method for obtaining high vacua in desiccators, which was invented by Benedict and Manning,<sup>1</sup> is shown by them to be of great value in the determination of water in foods and physiological preparations. The method consists essentially in expelling the air by evaporating ether in the desiccator under diminished pressure and subsequently removing the ether vapors by means of sulphuric acid. Vacua of less than 1 mm. of mercury are readily attained by this means.

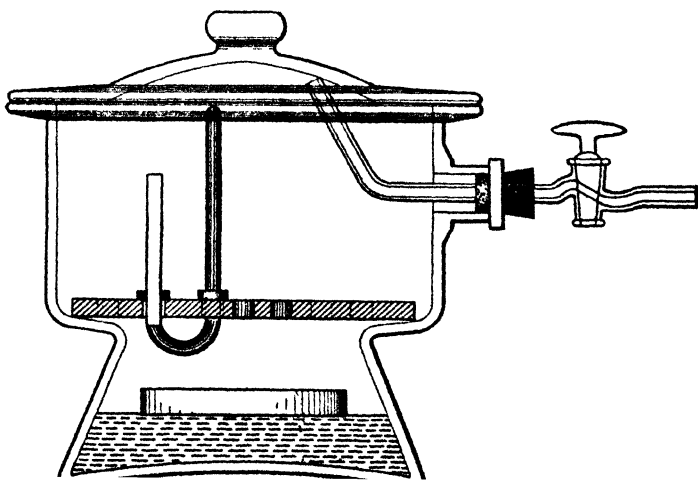
The Hempel desiccator, in which the sulphuric acid is located in the upper part of the apparatus, has been the type of desiccator mainly used by Benedict and Manning. The main objection to this form, in the opinion of the writer, and one which it is believed will prevent its general use, lies in the fact that the sulphuric acid is apt to spill, particularly at the time when the

<sup>1</sup> *Am. Ch. J.* 27, 340 (1902), and *Am. J. Physiol.* 13, 309 (1905).

upper compartment is removed.<sup>1</sup> In addition, it is a special form of apparatus not generally found in laboratories.

The Scheibler type of desiccator, in which, however, the sulphuric acid was contained in an acid dish in the upper part of the desiccator, was also used with success by the originators of the method. It is found by the writer that the Scheibler type works as well as the Hempel form and much more conveniently, when the sulphuric acid is contained in the *bottom* of the desiccator. Following are the details of the application of the ether-sulphuric acid method to the Scheibler desiccator in which the acid is contained in the bottom, together with results obtained in a comparison of the two types of desiccators.

A Scheibler desiccator of 20 cm. internal diameter is fitted with a one-holed new rubber stopper, through which passes a delivery tube reaching to near the top of the inside of the desiccator and terminating outside of the desiccator in a well-fitting stop-cock (best a stop-cock with a slant-bored hole). The rubber stopper before use is first well cleaned by being rubbed with a cloth moistened with chloroform, and then well greased with a mixture of vaseline and beeswax in which a little "pure gum" rubber tubing has been melted. The stop-cock is also lubricated



with this mixture. For the ground joint between the desiccator and its cover a vaseline and beeswax mixture is used. The

<sup>1</sup> It is found that the upper compartment of the Hempel desiccator is best loosened after the vacuum is destroyed, by driving the thin blade of a spatula between the ground surfaces by means of gentle tapping.



desiccator is provided with a simple U-shaped manometer, and charged with about 200 cc. of concentrated sulphuric acid on which is floated a Petri dish about 10 cm. in diameter (see <sup>\*</sup>drawing). Connection is made with the exhaust, best through two bottles (not shown in the figure), the first of which is arranged to act as a safety-bottle in case of back suction, and the second contains water in order that the outflow of gas may be observed.

When all is ready for the exhaustion, from 20 to 25 cc. of ether are added to the Petri dish, most conveniently through a long-stemmed funnel, the desiccator closed and suction applied. After the first rush of gas, a rapid, steady flow goes on as the ether evaporates from the Petri dish. The flow of vapors ceases as soon as the ether is volatilized and the stop-cock is now closed. The desiccator may now either be left to itself, when a gradual fall of the mercury in the manometer will be observed, reaching a minimum of about 1 mm. in a short time, or the apparatus may be gently moved about in such a manner that fresh surfaces of sulphuric acid will be exposed to the ether vapors. By the latter procedure a high vacuum is very rapidly attained. In case, however, materials are being dried which contain considerable quantities of water, loss by spattering may occur where the pressure is lowered so suddenly, and the former method is preferred. Such mechanical loss has been observed, for example, in connection with experiments in the drying of potato starch. When the pressure was very suddenly reduced from 50 mm. to 10 mm. or less, the water vaporized so suddenly that it carried the starch grains to all parts of the desiccator with almost explosive violence. The starch used contained only about 11 per cent. of water.

A set of experiments was carried out in which a Hempel desiccator, used according to the directions of Benedict and Manning,<sup>1</sup> and a Scheibler desiccator used according to the procedure given above, were run side by side. The material employed was a very pure sample of potato starch. Two-gram samples of the starch were weighed into small aluminum dishes, fitted with covers, of the kind recommended by Benedict and Manning.<sup>2</sup> The dishes with their contents were placed in the desiccators, their covers removed, and the process for obtaining the high

<sup>1</sup> Loc. cit.

<sup>2</sup> Am. J. Physiol. 13, 314 (1905).

vacuum applied to each desiccator. The desiccators were opened at the intervals indicated in the table. In opening, the air was admitted through a calcium chloride tube and the dishes were immediately capped with their respective covers and weighed. The percentages of water removed at the different intervals in the two desiccators are shown in the table below. The determinations were made in triplicate and the separate determinations in each set agreed closely throughout. The averages only are given in the table.

TABLE SHOWING THE DRYING OF STARCH IN HIGH VACUA IN HEMPEL AND SCHEIBLER DESICCATORS.

Desiccator	Time. Hours.	Per cent of water.
Hempel .....	30	10.20
" .....	74	10.67
" .....	146	10.69
Scheibler ..	24	10.58
" .....	68	10.74
" .....	140	10.76

The starch contained 10.90 per cent. of water, this determination being made by drying for two hours in a partial vacuum of about 60 mm. at 102° C.

The results show that the Scheibler form with the sulphuric acid in the bottom of the desiccator, equals the Hempel form as an apparatus for the rapid drying of materials in the high vacua obtained by the ether-sulphuric acid process.

A criticism of the ether-sulphuric acid process must be noted. There seems to be some slight tendency for the formation of acid fumes after the apparatus has remained evacuated for some days and a faint odor can be detected in the desiccator on opening. The dried starch samples from both desiccators were notably darker in color than the original sample, or the samples dried at 102°.

The method, therefore, cannot be recommended unqualifiedly, but it is the nearest approach yet made to an ideal method. The modification suggested in this paper is made in the hope that the method will be more widely adopted by chemists.

## A MODIFIED HYDROGEN SULPHIDE GENERATOR.

BY A. W. BROWNE AND M. F. MEHLING.

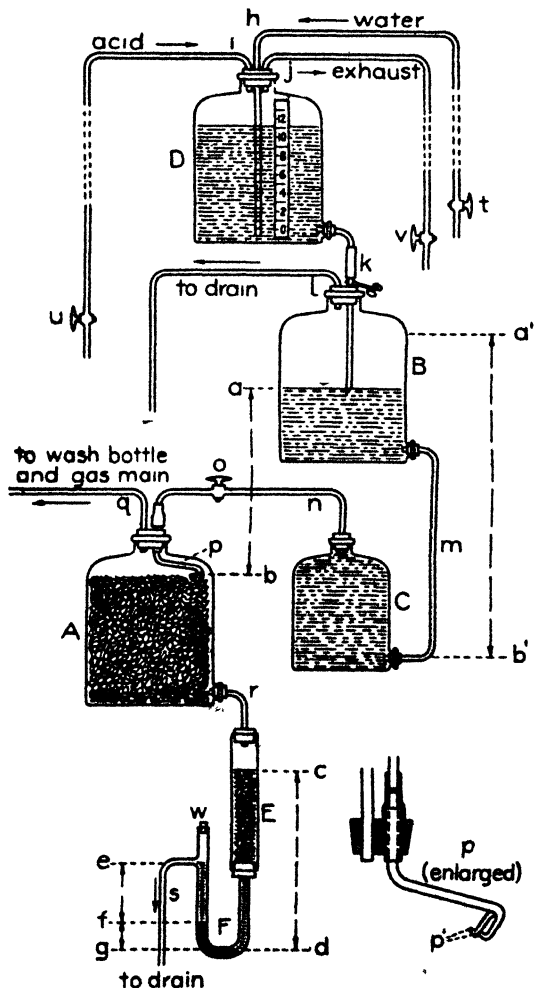
Received May 8, 1906.

IN 1892 Ostwald<sup>1</sup> described a gas generator of a type that has since been employed in more or less modified form by many teachers of analytical chemistry. For several years an apparatus of this sort has been put to a practical test in this laboratory, with the result that it has for our purposes proved unsatisfactory in at least four particulars. In the first place, the gas is not evolved at uniform pressure. The level of the acid in the uppermost bottle often undergoes appreciable change due to the alternate generation and utilization of an excess of gas. Aside from this oscillatory change in pressure there is also a continuous diminution in pressure, owing to the gradual consumption of the acid. Second, the progressive accumulation of spent acid in the lowest bottle materially diminishes the active surface of the ferrous sulphide. Third, the constant dropping of the acid upon one spot tends toward the formation of a cylindrical channel through the solid, with the result that the fresh acid has but little opportunity to act upon the solid before mixing with the spent acid below. And fourth, the apparatus requires entirely too much attention. This was found to be the case even when bottles capable of holding 25 kg. of ferrous sulphide and 14 liters of acid, respectively, were employed. It must be admitted, however, that the test to which the apparatus has been subjected was a rather severe one. Other well-known forms of apparatus have been subjected to the same practical test in this laboratory through a period of years, with equally unsatisfactory results. The elementary classes in analytical chemistry to be supplied in this laboratory with hydrogen sulphide contain from 175 to 275 students, of whom from 50 to 125 work in the laboratory at the same time, and the great majority of whom work in the laboratory at least nine hours per week. In order conveniently to supply classes of this size with an adequate amount of hydrogen sulphide it is essential that the generator should be capable of producing the necessary amount of gas under constant pressure, of regulating automatically the supply of fresh acid, and of effecting automatically the removal of the waste solution after the acid has been thoroughly neutralized.

<sup>1</sup> *Z. anal. Chem.* 31, 183 (1892); *Grundlinien der Anorg. Ch.* p. 282, (1904).

In attempting to modify the Ostwald apparatus so as to adapt it to the requirements of this laboratory, the authors have made free use of many suggestions contained in the literature of gas generators. Especial indebtedness to the excellent treatises of Küster,<sup>1</sup> Richards,<sup>2</sup> Bradley<sup>3</sup> and Parsons<sup>4</sup> must be acknowledged.

The apparatus finally adopted and tested during the past year is shown in the accompanying sketch. The tubulated bottles



<sup>1</sup> J. pr. Chem. [2] 48, 595 (1893); Chem. Ztg. 29, 158 (1905).

<sup>2</sup> Am. Ch. J. 20, 189 (1898).

<sup>3</sup> Ibid. 21, 370 (1899).

<sup>4</sup> This Journal, 25, 231 (1903).

A, B and C correspond with the main parts of the apparatus of Ostwald, Küster and Bradley. A and B each have a capacity of about 14 liters, while C is considerably smaller. Hydrochloric acid (prepared by diluting the concentrated commercial acid with an equal volume of water<sup>1</sup>) flows from B through m into C and then through n, o and p into the ferrous sulphide bottle A. The evolved gas passes through q into a wash-bottle containing water, and thence through a lead pipe to the hoods, where it may be obtained as needed by the students through 52 separate outlets. For the sake of economy, a device somewhat similar to that used by Parsons has been adopted, the flow of gas through the outlets being restricted to from 2 to 5 bubbles per second. Still further economy has been gained by insisting that precipitation shall be effected, whenever feasible, in closed flasks, somewhat after the manner suggested by Graebe.<sup>2</sup> The hoods and the generator itself are located in a separate room thoroughly ventilated by means of a fan operated by an electric motor. Leakage from the apparatus itself has been prevented by previously soaking all rubber stoppers and tubes in molten paraffin before wiring them in place.

The difficulties experienced with the Ostwald apparatus have been overcome as follows: In the first place, the oscillatory changes in pressure have been entirely obviated by causing the acid to fall upon the solid through two openings of small diameter. When the apparatus is furnishing but a small amount of hydrogen sulphide (as is the case for example when gas is being drawn from not more than 10 to 12 outlets at once), the acid slowly oozes from the two tips marked p', flows down the outside of the tubes, and finally drops from the two elbows (see enlarged sketch of p) upon the solid below. When the apparatus is suddenly compelled to furnish comparatively large amounts of gas, however (as is very often the case when, at the beginning of a period, gas is being drawn simultaneously from every outlet), the acid is automatically thrown out through the tips for a few seconds in two diverging streams. Thus a large surface of the solid is almost instantaneously moistened with the acid, and gas is at once evolved in considerable quantity. As soon as pressure equilibrium is restored, the supply of acid is automatically cut down to a speed depending upon the rate of consumption of the gas

<sup>1</sup> Sartorius: Chem. Centr. 1904, I, 246.

<sup>2</sup> Ber. 31, 2987 (1898).

by the students. Even if all outlets are suddenly closed at this time there is no appreciable excess of gas evolved. In fact, during the normal running of the apparatus, an excess of gas sufficient to force its way over into C or even up into p for any considerable distance is never evolved. It is obvious that the nicety of this automatic adjustment of the supply of acid must depend upon the promptness with which the acid and the solid react. After A has been freshly filled with ferrous sulphide the reaction takes place rather slowly, however, even though the solid has just been broken up, and may have many perfectly fresh surfaces. For one or two days after the semi-annual filling has been accomplished, the apparatus does not work at quite its normal efficiency, unless the precaution has been previously taken of permitting the ferrous sulphide to stand for a time in a solution of ferrous chloride, before subjecting it to the action of the hydrochloric acid.

The gradual diminution in pressure noticed with the Ostwald apparatus, and due to the consumption of the acid, has been prevented by using the tubulated, 14-liter bottle D. When all of the stop-cocks t, u and v on the glass tubes h, i and j are closed, the acid in D will flow out through the tube k only so fast as is necessary to keep the acid in B at the level a. Devices entirely similar in principle have of course long been used in other fields of work, and have been employed by Breyer,<sup>1</sup> Kalecsinszky<sup>2</sup> and Parsons for the maintenance of constant pressure in gas generators. In order to prevent the trapping of air bubbles it is important that the upper part of the tube k should not be exactly horizontal, but should slope downward at every point. The inside diameter of k should not be less than 1.5 cc. The tube l serves the purpose of carrying off fumes that may gather in B. It is open at the end, as atmospheric pressure should prevail in B. In our earlier experiments D was filled by pouring in water and acid by hand, after slipping a spring clamp over the short piece of rubber tubing at k, and was then tightly closed at the top by means of an unperforated rubber stopper. It was found possible to accomplish this rather disagreeable task much more rapidly and conveniently by means of an ordinary laboratory suction-pump. The glass tube h reaches to the bottom of a cylinder capable of holding about 6.5 liters of water, and placed con-

<sup>1</sup> Z. anal. Chem. 28, 438 (1889).

<sup>2</sup> Ibid. 31, 544 (1892).

veniently beneath a water tap. The glass tube *i* leads to the bottom of a carboy of concentrated commercial hydrochloric acid, while *j* communicates with a strong suction-pump. In order to fill *D* the suction-pump is turned on, the stop-cocks *t* and *v* are opened, and *u* is closed. After about 6.5 liters of water have been drawn in, *t* is closed, and *u* opened until the same quantity of acid has been introduced, when *u* is again closed. To insure thorough mixing of the acid and water *t* is now opened for a moment to permit air to bubble in through *h*, and is then closed, after which the spring clamp is slipped off from the rubber tube at *k*. One filling usually suffices to keep the apparatus running at constant pressure for at least one week, even when the class numbers about 275 students. When the class is smaller the supply lasts proportionally longer.

The second difficulty with the Ostwald apparatus was eliminated by effecting the continuous removal of the thoroughly neutralized spent acid. By the force of gravity the spent acid flows down through *r*, the inside diameter of which should be not less than 1.5 cc. in order to prevent the tube from acting as a siphon, or from being clogged with sediment. Care should be taken, moreover, not to have the upper portion of this tube exactly horizontal, but to have it slope downward at every point, in order to prevent trapping of gas bubbles. After passing through *r*, the spent acid enters *E*, a glass tube with an internal diameter of about 5 cm. This tube is filled with pieces of ferrous sulphide which serves the double purpose of thoroughly completing the neutralization of the acid, and of indicating in a general way the extent to which neutralization has been accomplished in *A*. Only very rarely may effervescence be seen to take place in *E* as the spent acid falls upon the solid. If, however, the level of the solid in *A* has been permitted to fall too low, or if for any reason the acid is cutting a channel through the solid in *A*, then a more or less brisk effervescence in *E* will call attention to the fact. From *E* the thoroughly neutralized acid flows by gravity into the U-tube *F*, which should have an inside diameter of not less than 2 cm. The right-hand end of this tube is sealed off, but is provided with two lateral openings each with a diameter of about 1 cm. This arrangement prevents clogging of the tube with small pieces of ferrous sulphide. The left arm of *F* is furnished with a side tube, *s*, through which the spent acid is finally carried to the

drain. The lower part of F is filled with mercury. This obviates the necessity of prolonging the left arm of F to a considerable elevation, and very effectively prevents the clogging of F with the fine material that gradually settles to the bottom, especially when the stop-cock o is closed and the apparatus allowed to remain inactive for some time. The apparatus has been permitted to rest in this condition for a number of weeks, and yet has not in any case shown the slightest sign of clogging when once more set in operation. The side tube s must enter F at a distance above the mercury sufficient to prevent loss of mercury globules thrown up by the occasional rapid bubbling of spent acid past the mercury. The amount of mercury to be used in F must obviously be governed by the following facts: The sum of the pressures represented by the vertical lines fg and ef must be greater than the pressure represented by a b, the normal pressure of the apparatus, in order to prevent loss of gas through F. It may also be made greater than the pressure represented by a'b' the maximum pressure theoretically obtainable in the apparatus in case an excess of gas sufficiently great to force all acid in C back into B should be generated. As a matter of fact, however, this condition is never even approximately realized in practice. Experiment has shown that even when a partial vacuum has been purposely established in A and E, the sudden opening of o does not admit sufficient acid to generate an excess of more than from 100 to 200 cc. of gas. The sum of the pressures represented by ef and fg must, moreover, be less than the sum of the pressures represented by a b and cd, in order that the spent acid may flow out. The level c of the spent acid may be changed at will, without varying the pressure in A, by changing the amount of mercury in F. This is readily accomplished by means of a pipette introduced through the aperture w, which is ordinarily closed by means of a rubber stopper. By increasing the amount of mercury in F the level c may be raised until it reaches any desired point within A. If it should be desired to simplify the overflow apparatus, E could be dispensed with entirely, and a single tube could be used to replace r and F. In this case it would be advisable to introduce a sufficient quantity of mercury to raise the level c to a point about one-fourth of the distance from the bottom to the top of A. In our experience it has been found almost impossible to effect complete neutralization of the acid without permitting it to remain in contact with the solid for some little time.



The third difficulty enumerated in the opening paragraphs was overcome with the aid of the double dropper, p, to which reference has already been made. The use of this device has greatly lessened the tendency toward the formation of channels in the solid. If the apparatus is but rarely required to supply large amounts of gas, however, the acid always slowly drops from the two elbows, and may in time produce channels, particularly if the pieces of ferrous sulphide are small. Trouble from this source may be quickly remedied by grasping the tube p at the point where it emerges from A beneath the rubber tubing, and twisting it around through an angle of about  $90^\circ$ . This operation is rendered very simple by the fact that p does not actually touch the rubber stopper through which it passes, but is encased in a short close-fitting piece of glass tubing as shown in the enlarged sketch. In our work it has been found sufficient to twist p two or three times during the course of the term's work.

The extent to which the fourth difficulty has been overcome may be inferred from the following statements: One filling of the ferrous sulphide bottle usually suffices for an entire term's work. The only daily task of the attendant consists in opening the stop-cock o at the beginning, and closing it at the end of a laboratory period. Even this precaution is not necessary, except to prevent leakage of gas through outlets inadvertently left open by the students. The acid bottle D is filled at intervals of from one to two weeks, as stated above. This operation is accomplished semi-automatically, involves no handling of acid, and requires but a few minutes of time. Moreover, no fumes, either of hydrochloric acid or of hydrogen sulphide, are permitted to escape into the room. To supply a class of 180 students during one term's work, the consumption of one carboy (50 liters) of commercial hydrochloric acid and about 23 kg. of ferrous sulphide was found to be necessary.

#### SUMMARY.

By modifying the Ostwald gas generator in the manner indicated in the preceding pages an apparatus possessing the following advantages may be constructed.

(1) It readily furnishes hydrogen sulphide in quantities sufficient to supply a class numbering 275 students, provided that the gas is made to bubble through the 52 outlets at a rate of from

2 to 5 bubbles per second, and provided that precipitation is usually effected in closed flasks.

(2) The gas is evolved at uniform pressure whatever may be the rate of its consumption, provided only that this rate does not exceed the maximum rate of generation of which the apparatus is capable.

(3) One charge of ferrous sulphide usually suffices for a term's work. The removal of a single rubber stopper permits the introduction of a new charge.

(4) One charge of acid (1:1 hydrochloric) suffices for a period of from one to two weeks. The charge may be renewed at any time without manual labor, by the simple manipulation of a few stop-cocks.

(5) No fumes, either of hydrogen sulphide or of hydrochloric acid, can escape into the air at any time except to some extent during the semi-annual renewal of the charge of ferrous sulphide.

(6) The spent acid is automatically discharged without changing the pressure in the apparatus, and not until it has stood in contact with ferrous sulphide for a sufficient length of time to insure its complete neutralization.

(7) The stop-cock o may be discarded entirely if this is desirable. The actual working parts of the apparatus will then be devoid of stop-cocks, as t, u, v and the pinch-cock at k are used solely for the purpose of filling D.

(8) Since the apparatus is made of glass parts, its condition at any time may be seen at a glance.

(9) The apparatus may be set up without difficulty by anyone who has had a little experience in amateur glassblowing. The tubulated bottles are ordinarily carried in stock by manufacturers of laboratory apparatus.

The authors wish to express their gratitude to Professor L. M. Dennis for the interest he has taken in their work and for the helpful suggestions he has given them.

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## AN ELECTRICAL RESISTANCE FURNACE FOR THE MEASUREMENT OF HIGHER TEMPERATURES WITH THE OPTICAL PYROMETER.

BY ALEXANDER LAMPEN.

Received May 16, 1906.

THE plan adopted was to heat a small quantity of the material or substances under investigation to a required temperature, and after being kept at this point for a certain time, withdraw and examine it for any physical or chemical change taking place, and then if necessary place again in the heated zone of the furnace, the temperature of which was raised to a known degree.

By repetition of this operation with an increase of temperature by known intervals the desired change in the material could be reached with an approximate knowledge of the temperature which had produced this change.

Such a furnace should fulfil the following requirements:

(1) To consist of materials which should withstand a sufficiently high temperature without destruction.

(2) The temperature zone to which the substance is exposed should permit a variation to wide limits, and be easily regulated.

(3) To enable a direct measurement of the temperature of the substance by sighting with an optical pyrometer on it, or on a surface raised to the same temperature.

(4) To enable an easy and rapid removal and replacement of the substance during the run.

(5) To come as nearly as possible to the optical properties of a "black body."

As it was desired to work up to temperatures of approximately 2500° C. the only available material for the furnace was carbon. From the ease with which Acheson graphite can be machined, this article was exclusively used for the construction of the working parts of the furnace.

After several experiments with furnaces of varying construction, the plan finally adopted was that shown in Fig. 1. The enclosing walls *A* of fire-brick were lined with a mixture *B* of equal parts of fire-clay and siloxicon to prevent fusing. The terminals, *C*, were Acheson graphite electrodes, the outside parts of which were wrapped with sheet asbestos *I*, to prevent oxidation.

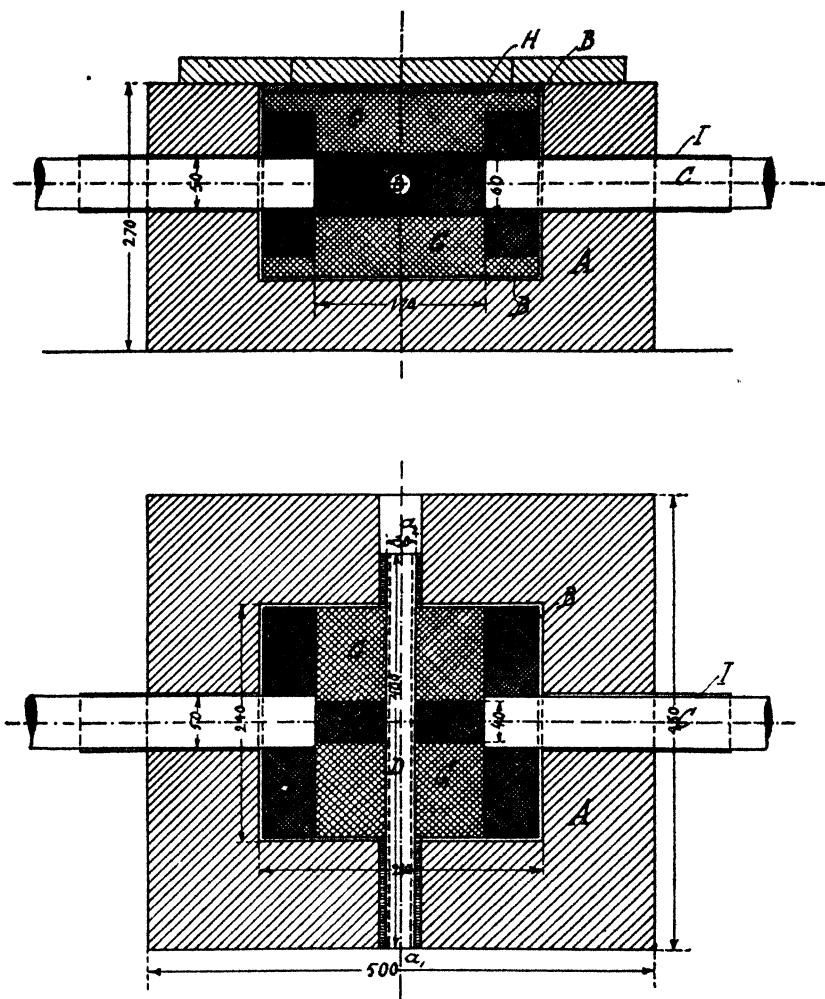


Fig. 1.

A graphite tube, *D*, 400 mm. long, 30 mm. outside, and 23 mm. inside diameter, was placed transversely across the furnace, through holes provided in the walls. The ends of this tube were also wrapped in sheet asbestos, and luted with the above mixture.

The tube was so placed within the asbestos bushings that it allowed of expansion without tending to fracture.

The core, *E*, and the layer, *F*, around the free ends of the terminals, *F*, consisted of powdered coke.

The filling mass, *G*, was crushed charcoal and on top of this was

a thin layer of carborundum,  $H$ , in order to prevent the burning of the charcoal. The furnace was covered with fire-bricks, and the walls carefully luted with fire-clay to keep the air out of the inner parts.

Fig. 2 gives the necessary details of the working parts.  $D$

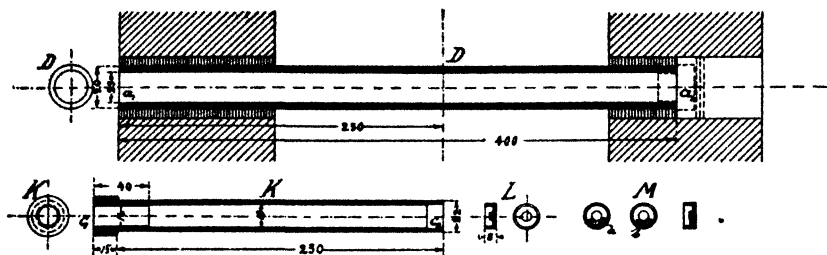


Fig. 2.

is the transversal tube. The substance which is to be heated is introduced into a small graphite capsule,  $L$ , and then placed in the end,  $c_2$ , of a second tube,  $K$ ; this is then slipped into tube  $D$  at  $a_1$ . The diameter of tube is of such size as to slip easily within tube  $D$ .

When the current is passed through the furnace the hottest part of the fixed tube will be in the core, and the temperature decreases towards the ends. By regulating the current, and moving the sliding tube,  $K$ , in a proper manner, the desired temperatures may be easily reached and maintained.

The temperature readings are taken through the end,  $c_1$ , by sighting with the pyrometer on the capsule. To remove the substance the sliding tube is pulled out and the capsule removed with a carbon rod. During the runs the end,  $a_2$ , of the tube  $D$  was shut with a well-fitting graphite plug and the opening in the wall closed with asbestos and luted with fire-clay to prevent air circulating in the tube.

The substance was introduced into the capsule so that it occupied the lower part of it only as seen at  $M$  (Fig. 2).

When in powder it was slightly packed to a layer of 0.5 to 1 mm. thickness ( $a$ ); if in lump, a piece of the same thickness was placed as indicated by  $b$ .

This was in order to get uniform readings as the upper half of the capsule supplies the light for the pyrometer field, and thus radiations from a graphite surface were investigated independent of the substance which was heated.

The choice of the material,  $G$ , for filling was somewhat restricted as it was essential that it be a poor conductor of heat and electricity and should not contain constituents which on decomposition by heat would give rise to fumes, and thus interfere with pyrometer measurements, and should stand the highest temperatures without fusing or reacting upon the graphite tube.

Many different materials were tried for this purpose, and charcoal was found to be the only one fulfilling these requirements.

The length of the fixed tube,  $D$ , was a matter of considerable importance, because that portion passing through the charcoal  $G$ , should be long enough to admit a considerable drop of temperature from the core, and also the end,  $a_1$ , must be far enough from the centre of the heat so that it can be kept below a red heat. In spite of this some oxidation at the mouth of the tube did take place, which could be probably entirely avoided by using some water-cooling device at this point. The inner tube,  $K$ , was coated with a thin layer of siloxicon two-thirds of its length from  $c_1$  to prevent its oxidation when removed hot from the furnace.

The currents used were alternating, 150-450 amperes at 15-20 volts.

During the first runs of a new furnace some difficulty was experienced from fumes in the tube interfering with the pyrometer observations. These were probably derived from decomposition of impurities in the tube or the surrounding bodies. After a few runs these fumes were no longer observed, the impurities which gave rise to them having been volatilized.

In order to ascertain how much the radiation from the capsule differed from that of a black body a series of comparative temperature measurements were made with a Wanner optical pyrometer and a Siemens and Halske thermocouple. The latter instrument was standardized up to about  $1050^{\circ}\text{C}$ . and had a scale up to  $1400^{\circ}\text{C}$ . The couple was introduced into the sliding tube, the temperature regulated and kept constant for a while, the couple then quickly removed and a reading taken with the optical pyrometer. The current which supplied the standard lamp of the Wanner instrument was kept constant by means of a rheostat and milliammeter.

TABLE I.

The junction of the couple bare and nearly touching the capsule.

Siemens and Halske.	Wanner.
1105 C	1116 C
1135	1142
1175	1183
1205	1208
1210	1211

TABLE II.

The junction of couple placed in a clay tube, the bottom of which was about 1 mm. thick and in contact with the capsule.

Siemens and Halske.	Wanner.
1275	1296
1310	1330
1373	1388

As far as these results go, it shows that the optical properties of the apparatus did not deviate appreciably from those of a "black body."

The method of carrying on the observations was as follows:

The sliding tube provided with an empty capsule was introduced into the furnace, the current thrown on, and the temperature readings taken at intervals. When the temperature of the centre of the furnace had become somewhat higher than the desired temperature the tube was removed and the empty capsule replaced with one charged with the substance under investigation. The sliding tube was now gradually pushed into the fixed tube, all the time following the rising temperature with the pyrometer, until the desired point was reached, and this temperature was maintained by slight alteration of the position of the inner sliding tube. If the pyrometer gave any indication of a tendency to rise above this point, the sliding tube was withdrawn a short distance and *vice versa*. After a sufficient time the sliding tube was gradually pulled out to give it time to cool, the capsule removed, examined and replaced, or another capsule ready charged introduced and heated as above described. The removing, replacing and reheating could be carried out in from three to five minutes. It will thus be seen that a great many determinations can be made in a comparatively short time.

The following examples illustrate the mode of working and the results obtained:

#### SILICON CARBIDE.

A mixture of sand and coke corresponding to the reaction  $3C + SiO_2 = 2CO + SiC$  was reduced to fine powder and raised to

the temperatures as given below. To determine when the reaction had taken place, the mixture was heated over a Bunsen burner to remove excess of carbon, and then treated with boiling concentrated hydrofluoric acid to remove the unchanged silica. The resulting greenish gray amorphous residue indicated the presence of silicon carbide.

TABLE III.

Temperature	Time of heating.	Results.
1500	5 minutes	Sintered, no reaction.
1500	10 "	"
1540	10 "	"
1600	10 "	Traces of carbide.
1700	10 "	More carbide.
1800	10 "	Homogeneous mass, mostly carbide.
1900	10 "	Homogeneous mass, mostly carbide.
2000	10 "	Small crystals in amorphous mass.
2100	10 "	Mass of crystals.

Some carbide crystals (carborundum) were introduced and heated as follows:

2100° C.	10 minutes	No change.
2200	10 "	"
2240	10 "	Graphite.

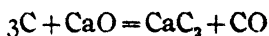
This shows that the reaction point between the above substances is somewhere round 1600° C. The formation of crystallized carbide or carborundum begins between 1900 and 2000° C. and its decomposition into silicon and graphite between 2200° and 2240° C.

The former point had been previously determined in this laboratory to be 1940° C. and the latter 2220° C.

In order to determine more closely the reaction point between carbon and silica, a mixture of pure materials was prepared and heated with small temperature intervals. The first indications of the reaction could be detected at 1615° C., whereas at 1600° C. no carbide could be found with certainty.

#### CALCIUM CARBIDE.

A fine powdered mixture of coke and calcium oxide (commercial) according to the reaction



was heated at 100° C. intervals for ten minutes.



TABLE IV.

Temperature.	Results.
1500° C.	Slightly shrunk, no gas on addition of water.
1600	More shrinkage, no gas.
1700	Gas evolved with water, an odor of crude acetylene.
1800	The mass fused, abundance of gas with water.

Next, a piece of commercial calcium carbide was heated to:

1750° C.	Traces of sintering.
1780	Partly fused.
1800	Completely fused.

A proper mixture of pure calcium oxide and carbon was heated at small temperature intervals for ten minutes. The presence of calcium carbide was determined by dropping a piece of the mixture into ammoniacal cuprous chloride solution, which gives a red precipitate with acetylene.

TABLE V.

Temperature.	Results.
1700° C.	No carbide detected with certainty.
1725	Traces of carbide.
1740	More carbide.

#### MELTING TEMPERATURES OF SOME REFRACTORY MATERIALS.

A rough determination of the melting-points was carried out for a number of refractory materials used in this laboratory.

TABLE VI.

Fire-clay (Henry Maurer, N. Y.):	
1350° C.	No change.
1400	Fused down.
Fire-brick (Henry Maurer No. 2 A.):	
1550° C.	Partly fused.
1600	Completely fused.
Porcelain from crucible (Dresden):	
1600° C.	Edges rounded.
1650	Fused down.
Piece of pure quartz:	
1650° C.	Edges rounded.
1700	Fused.
Magnesia brick with high percentage iron:	
1900° C.	Edges rounded.
2000	Completely fused.
Magnesia fused in electric arc:	
2000° C.	Fused.

During the work it was found that covering the end of the sliding tube with a red glass of sufficient thickness, most of the substances under examination could be clearly seen against the surface of the capsule. This is due to the fact that their radiating power is less than that of carbon, and also because the temperature of the free surface must be somewhat lower than that of the capsule. This provided a means of observing the change of form, to some extent at least, of the heated substance, and to recognize a sintering or fusing of the substance without removing the capsule. The presence of the fumes which were occasionally developed by decomposition of the substance could also be detected in the same way.

ELECTROCHEMICAL LABORATORY, COLUMBIA UNIVERSITY,  
March 15, 1906.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 125].

## THE MEASUREMENT OF TEMPERATURE IN THE FORMATION OF CARBORUNDUM.

BY S. A. TUCKER AND ALEXANDER LAMPEN.

Received May 16, 1906.

THE purpose of this investigation was to determine, if possible, the temperature for the formation of carborundum, and its decomposition into graphite and silicon.

When a carborundum furnace built on the lines of a commercial furnace was taken down after a run it was found that fairly sharp lines of demarkation could be observed between the layers of graphite, carborundum (crystallized silicon carbide), and siloxicon (amorphous silicon carbide). If after bringing the furnace to a stationary condition, temperature measurements could be made at different points of the cross-section, the desired temperatures could be easily obtained.

This was accomplished by placing through the centre of the furnace a horizontal graphite tube containing a plug which could be pushed to any desired section and its temperature measured by an optical pyrometer.

### THE FURNACE.

This, as will be seen from the drawing (Fig. 1), was built on the general plan of a furnace used in the manufacture of carborundum,

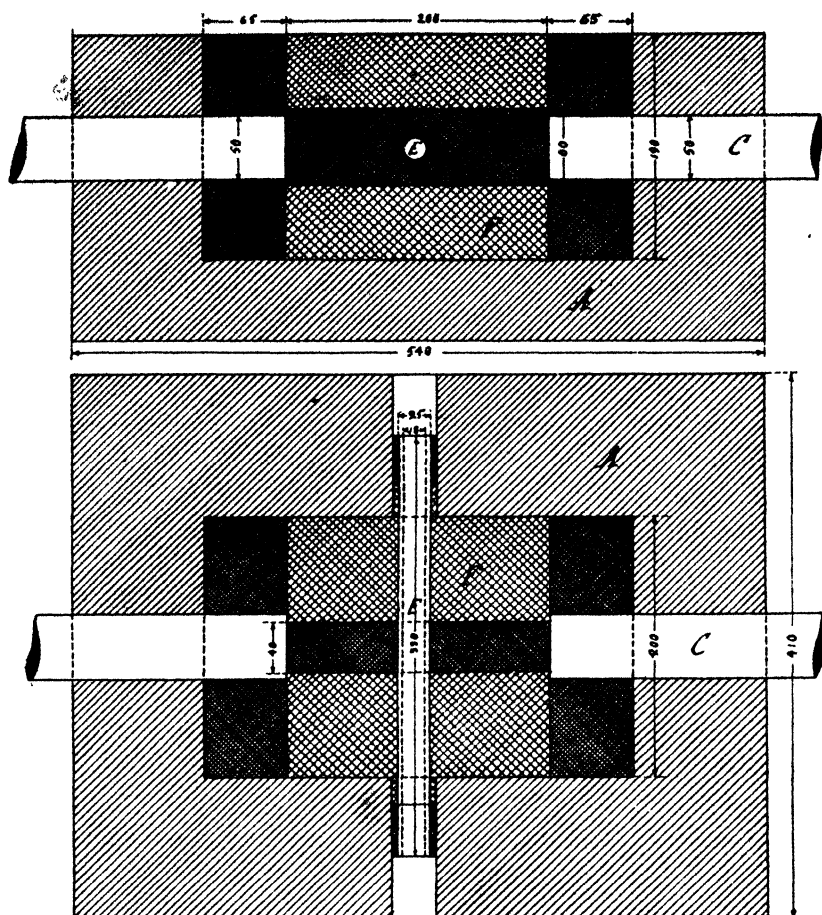


Fig. 1.

though several alterations were made in the proportions of the furnace as well as the dimensions and the form of the core, owing to the voltage used and the particular use to which the furnace was to be put.

After several experiments the following construction was adopted:

The retaining walls of fire-brick, *A*, enclosed a space 330 mm. long, 200 mm. wide, and 190 mm. deep. The terminals of Acheson graphite, *C*, were 50 mm. in diameter and placed at a distance of 200 mm. between the ends. A tube, *E*, bored out of Acheson graphite, with a length of 330 mm., and outside diameter of 25 mm., and inside diameter of 18 mm., was put transversely

through the centre of the furnace with the ends projecting into holes provided in the brick retaining walls and luted with fire-clay. Thin plates of sheet iron were placed against the ends of the terminals which were surrounded with a packed layer of powdered coke, *D*. The space between the plates was filled with charge *F*, to a proper height, and a core of powdered coke, *B*, 40 mm. wide and 60 mm. deep was made between the terminals by means of iron plates. The furnace was then filled up with the charge and all the plates withdrawn. The charge, of which about 8 kilos was used, consisted of:

Coke .....	34.2 parts by weight.
Sand .....	54.2 " " "
Sawdust.....	9.9 " " "

Finally a graphite plug 17.5 mm. in diameter and 9 mm. long was slipped into the tube and the furnace was ready for a run.

It was found after several preliminary trials that a good yield of carborundum could be obtained with 12 kilowatts running about two hours.

#### PYROMETER.

This instrument was by Wanner, and was used with all the precautions indicated by Waidner and Burgess in their work on optical pyrometry.<sup>1</sup>

The current which supplied the standard electric lamp was kept constant by means of a milliammeter and variable resistance throughout the work. Before using the instrument it was checked up with a standardized thermocouple to temperatures around 1300° C. and was found to vary but slightly. At the higher temperatures a black glass is interposed between the instrument and the incandescent body, and this point was found to be in close agreement with the open instrument. It may be said that on using the instrument without control of the current which supplies the standard lamp, no accurate measurements can be obtained.

#### EXPERIMENTAL.

The run is started with 130 volts alternating current, the maximum voltage of the generator. The current is hardly appreciable at first but as the resistor begins to warm up gases are evolved, and should be lighted at once to prevent explosion.

<sup>1</sup> "Optical Pyrometry," by C. W. Waidner and G. K. Burgess, Bureau of Standards, Washington, D. C., 1905.

Some time is taken in getting the current to the required point by varying the field of the alternator.

The pyrometer was set up in a fixed position so that by sighting through one end of the graphite tube the radiations from the plug would illuminate the field completely.

The first run made in this way had for its object the determination of the maximum temperature of the furnace which would give a good yield of carborundum, and clearly defined layers, and was found to be about  $2300^{\circ}$ .

If too high a temperature is attained, the layers will, of course, be pushed further to the sides of the furnace, and fusion of the retaining brick walls is likely to result, which changes the shape of the furnace to such an extent that no properly defined layers can be distinguished. Therefore, in the succeeding experiments the temperature of the furnace was raised until the plug in the centre of the core indicated a temperature of nearly  $2300^{\circ}$  C. and this temperature maintained constant for this point throughout the run.

The temperature was slowly raised during about two hours and then kept at its maximum until the condition of the furnace could be considered stationary, *i. e.*, the reaction practically finished and the layers fixed. The decreasing evolution of gases indicated when this point was reached. Then the plug was pushed by means of carbon rods to the desired position and given time to acquire the surrounding temperature. The pyrometer was sighted on it and the temperature recorded.

Between readings the ends of the tube were closed with pieces of sheet asbestos.

The following table shows the results of a run as recorded:

Time.	Volts.	Amperes.	Position of the plug.	Temperature.
10.25	130	.....	Centre	.....
10.50	55	130	"	.....
11.00	47	205	"	1664° C.
11.10	45	230	"	1766
11.20	44	240	"	1865
11.25	42	260	"	2030
11.30	42	260	"	2120
11.35	41.5	270	"	2175
11.40	41	265	"	2175
11.45	41	280	"	2175
11.50	41	300	"	2270
11.55	40.5	300	"	2250
12.00	40.5	300	"	2260

Time.	Volts.	Amperes.	Position of the plug.	Temperature.
12.05	40.5	300	Centre	2270
12.09	40.5	300	2 cm. from centre.	2248
12.13	40.5	305	3 cm. " "	2205
12.18	40.5	300	5 cm. " "	2088
12.23	41.0	300	7 cm. " "	1925
12.29	41.0	300	9 cm. " "	1758
12.32	41.0	295	Centre.	2260
12.39	41.5	290	2 cm. from centre to other side	2236
12.41	42.0	295	3 cm. " "	2194
12.47	42.0	290	5 cm. " "	2073
12.52	42.0	285	7 cm. " "	1897
1.06	43.0	290	9 cm. " "	1740

After cooling, the furnace was taken down and a section made, exposing the tube on which measurements of the positions of the layers were then taken. These measurements defining the limits of the different products combined with the temperature measurements in the above table resulted in the following curve (Fig. 2):

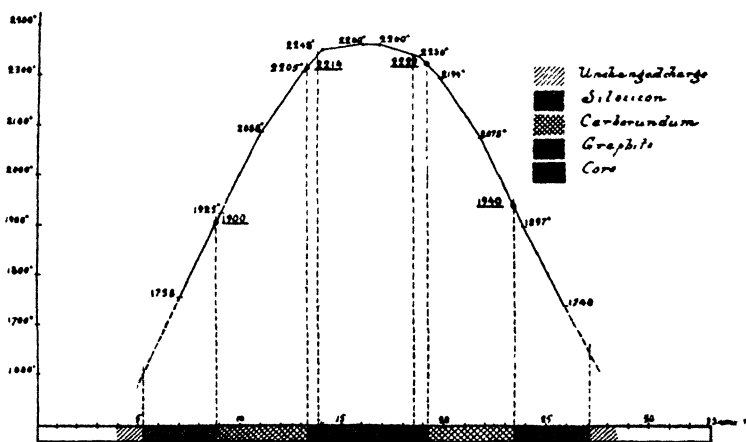


Fig. 2.

This curve gives as the decomposition temperature of carborundum into graphite and silicon  $2218^{\circ}\text{C}.$ , and as its formation temperature, *i. e.*, the point where the amorphous turns into crystalline, about  $1920^{\circ}\text{C}.$  From another experiment the decomposition point of carborundum was found to be  $2223^{\circ}\text{C}.$ , and the formation point  $1980^{\circ}\text{C}.$  The line between silicon and carborundum is always less defined than that between carborundum and graphite. This explains partly at least, the variations in the determinations of the latter point. As a limit was

considered the section where crystals could yet be found in the amorphous mass.

As an average may be taken for the formation point of carborundum  $1950^{\circ}\text{C}$ . and as its decomposition point into graphite and silicon  $2220^{\circ}\text{C}$ .

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## VOLUMETRIC METHOD FOR THE ESTIMATION OF CARBON IN IRON AND STEEL WITH THE USE OF BARIUM HYDROXIDE.<sup>1</sup>

BY JAMES A. AUPPERLE.

Received May 16, 1906.

THE method which I am about to describe has been found to compare very favorably with results obtained by gravimetric methods, with the advantage of being more rapid. It is based upon the following data:

*First.*—Barium hydroxide can be titrated with acids in the presence of barium carbonate (which is neutral or faintly alkaline to phenolphthalein), and no carbonic acid will be lost.

*Second.*—Carbonic acid is indicated by phenolphthalein, and when any barium carbonate is dissolved by standard acid during titration, the fact will be shown by the change in color.

*Third.*—Barium hydroxide can be titrated with acids without filtering off the barium carbonate, providing the acid is run into the mixture by a prolongation of capillary tube attached to the burette and extending well into the solution that is being titrated.

The reason for using the capillary tube is that if any carbonic acid be liberated in the lower portion of the beaker, it would be reabsorbed by the upper portion containing barium hydroxide.

Hydrochloric acid has been found to give the best results, and an acid a trifle less than  $\text{N}/5$  is used. This is prepared by mixing 15 cc. of acid (1.20) and 1000 cc. of water. One cc. will approximately equal 0.001 gram carbon.

The barium hydroxide solution is prepared from 31.5 grams of Merck's crystallized salt ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) dissolved in 1000 cc. of boiled water. When both acid and alkali are at room temperature, and without waiting for the suspended barium carbonate to settle completely, a measured portion is titrated with acid, and the remaining barium hydroxide is then diluted with water,

<sup>1</sup> Read before the Indiana Section of the American Chemical Society at Lafayette, Ind., May 12, 1906.

so that 1 cc. = 1 cc. of acid. The barium hydroxide is then allowed to stand until clear, and again titrated with acid.

The phenolphthalein solution is 1 to 30 of alcohol, and as it usually contains acid, it is rendered pink with dilute caustic soda or potash. Three drops of phenolphthalein are used for each titration.

When sulphuric or oxalic acid is used for titrating, the barium sulphate or oxalate formed in addition to the barium carbonate present, renders them less desirable than hydrochloric acid, which forms no precipitate.

In using this method in connection with burning steel filings in a current of oxygen, an accurate determination of carbon can be made in twenty minutes, which includes the time consumed in filing the steel.

I have found that filings carefully taken, check well in carbon, as found in borings secured in the usual manner, with the advantage that an ignition can be made at a lower temperature and in less time.

The following table will show how the time is distributed in making a direct combustion.

	Minutes.
Filing the sample.....	4
Weighing sample and placing dish in Aupperle combustion crucible .....	2
Measuring barium hydroxide, attaching Meyer tube to combustion apparatus, starting oxygen and lighting gas.....	3
Ignition of borings.....	8
Emptying, washing bulb and titrating.....	3
	<hr/> 20

In filing the sample, a large file which has been previously cleaned with a stiff brush is used. The filings are weighed and placed in a platinum dish that fits the Aupperle crucible. This dish contains a  $\frac{1}{8}$  inch layer of 120 mesh emery which is heavier than the precipitated alumina ordinarily used and is not so easily projected out of the dish.

The platinum dish is covered with a disk of platinum foil perforated in two semi-circles which form wings, one bent into and the other out of the dish. The wings are bent at angles of  $45^\circ$  which prevent anything being projected out of the dish.

I have found that with two ounces of gas pressure and gas averaging 700 B. T. U. per cubic foot the crucible becomes white



hot, and steel filings are completely oxidized in eight minutes. A Bunsen vertical blast-lamp gives good satisfaction.

At least twenty pounds of air pressure should be used. A single cylinder compressor making 150 revolutions per minute gives enough air for two lamps. By simply closing the valve through which the air enters the pump, a five-pound vacuum can be maintained and used for suction filtering.

Mr. Philo Kemery, of the Crescent Steel Works, Pittsburg, devised the spiral educt tube of the Aupperle crucible which I have adopted and found very satisfactory. The present form of the crucible has one coil of the educt tube around the crucible and joined to the side instead of the bottom. This permits more heat to be concentrated on the bottom of the crucible, and the educt tube becomes hot enough to oxidize all carbon to carbon dioxide.

The standard barium hydroxide and standard acid are contained in bottles holding twelve liters, each bottle being supplied with compressed air in order to facilitate rapid measuring.

The air that enters the barium hydroxide bottle is passed through a solution of caustic potash.

The capillary tube attached to the burette stop-cock is about five inches long.

For carbon determinations in steel 75 cc. of barium hydroxide are used, but for iron 150 cc. contained in two Meyer tubes should be used, each containing 75 cc. The second tube will only show a precipitate of barium carbonate when a very rapid current of oxygen gas is used, or when the sample is extremely high in carbon. Iron borings should be ignited for twelve to fifteen minutes, and the oxide of iron remaining in the dish should be fused into one globule. The original shape of the borings should then have entirely disappeared.

The barium hydroxide and carbonate are poured into a beaker, and the Meyer tube rinsed three times with boiled distilled water. Three drops of phenolphthalein indicator are added and standard acid run in very rapidly until the red color disappears and the white barium carbonate is seen. The beaker is then removed and placed under a burette containing standard barium hydroxide, which is added slowly, and until the original red color returns. The number of cubic centimeters barium hydroxide

used in titrating back is subtracted from the acid burette reading. Only about 1 cc. is usually required.

In experimenting to find how much carbon dioxide would be lost by adding sufficient standard acid to dissolve all the barium carbonate, and immediately titrating back with barium hydroxide, 75 cc. of acid were added to the mixture of barium hydroxide and carbonate from a 0.90 per cent. carbon steel, and on titrating back to original pink 0.88 per cent. was found, thus showing practically no loss of carbon dioxide even when all barium carbonate is dissolved.

The acid is standardized with steel or iron of known carbon content. For steel the theoretical value may be used, 1 cc. N/5 acid = 0.0012 gram carbon. The following table shows how well the method checks with the gravimetric methods.

	Weighing as BaCO <sub>3</sub> . Gravimetric. 3-Gram samples.	Volumetric. 3-Gram samples.	
Steel standard .....	0.090	0.090	
" " .....	0.115	0.113	
" " .....	0.380	0.393	
" " .....	0.643	0.627	
" " .....	0.735	0.725	
	1-Gram samples.	1-Gram samples.	
" " .....	0.890	0.890	
" " .....	1.130	1.150	
" " .....	1.350	1.330	
Iron .....	2.89	2.93	
" .....	3.30	3.35	
International standard...	3.25	3.31	
" " .....	3.67	3.65	
Iron .....	3.76	3.72	
" .....	4.30	4.32	

The following results are reported by Mr. J. C. Dickson of the Inland Steel Co., Indiana Harbor, Ind., to whom I extend thanks for investigating this volumetric method.

	Gravimetric method by KOH.	Volumetric.
Steel.....	0.463	0.460
" .....	0.890	0.896
" .....	0.934	0.929
" .....	1.097	1.101

To show that practically no barium carbonate dissolves during titration, several samples, after being titrated, were filtered and the barium carbonate weighed with the following results:

	Volumetric method.	Gravimetric after titration.
Carbon.....	0.89	0.88
	0.97	0.97
	2.73	2.75
	2.75	2.80
	3.17	3.20
	3.58	3.59
	3.84	3.83

Many chemists prefer burning the carbonaceous residue, and I have found that graphite is rapidly oxidized if filtered on a small Gooch crucible and then without drying or removing the asbestos, the Gooch is immediately placed *bottom up* in the combustion crucible. Fifteen minutes burning will be ample time using about 60 cc. oxygen gas per minute.

I wish to avail myself of this opportunity to thank Mr. H. A. Schwartz, the Secretary of the Indiana Section of the American Chemical Society, for investigating synthetic mixtures of various amounts of dried, and also freshly precipitated barium carbonate, when mixed with various amounts of standard barium hydroxide and titrated with acid.

The Aupperle crucible is described in *Iron Age* of October 6, 1904; abstracted in *Iron and Steel Magazine*, December, 1904.

LABORATORY OF E. C. ATKINS & CO.  
INDIANAPOLIS, IND.

## THE DETERMINATION OF CARBON IN IRON AND STEEL BY DIRECT IGNITION WITH RED LEAD.<sup>1</sup>

BY CHARLES MORRIS JOHNSON.

Received January 22, 1906

THE writer's experience with this method for the determination of carbon, together with some notes on what led to its adoption for routine combustion analysis, may prove of interest.

The solution of steel drillings containing large percentages of chromium, tungsten or molybdenum in double chloride of copper and potassium causes more or less loss of carbon as hydrocarbon. Especially sensitive to such loss are the carbides that are separated by the double chloride from steels in which are 10 or 12 per cent. of molybdenum together with several per cent. of chromium.

These carbides may lose some of the carbon by contact with

<sup>1</sup> A preliminary paper was read at the December meeting of the Pittsburgh Section of the American Chemical Society.

dilute acid, or with the oxygen of the air during washing with *suction* or during the subsequent drying of the carbide at the temperature of boiling water.

In the spring of 1900, the writer made an analysis for carbon of a steel containing 3.8 per cent. of chromium, applying the ordinary method of dissolving the borings in acid double chloride of copper and potassium, filtering on an asbestos plug, washing the carbide residue alternately with distilled water, and a mixture of one part of hydrochloric acid and twenty parts of water. The residue was then washed with water, alone, to remove the acid. After drying the washed carbide in a water oven, it was burned with purified oxygen in a red hot porcelain tube containing about 13 cm. of copper oxide. The products of the combustion were passed through granulated zinc of 20-mesh fineness, then through anhydrous calcium chloride, and then through phosphoric anhydride. The purified carbon dioxide was absorbed and weighed in potash bulbs. Duplicate analyses by this method failed to check.

A series of analyses of these borings were made. The acid wash *when used* was alternated with distilled water and the washing was then completed with distilled water, alone, to remove acid.

	Kind of wash.	Number washings.	Carbon found. Per cent.
1.....	20 parts H <sub>2</sub> O to 1 part HCl	20	1.65
2.....	100 parts H <sub>2</sub> O to 1 part HCl	20	1.52
3.....	100 parts H <sub>2</sub> O to 1 part HCl	2	1.909
4.....	100 parts H <sub>2</sub> O to 1 part HCl	2	1.943

In August, 1902, the process used in the foregoing, (3) and (4), was applied to a steel containing 4 per cent. of chromium and 4 per cent. of molybdenum with the following absence of agreement:

First analysis gave 1.28 per cent. carbon.  
 Second analysis gave 1.53 per cent. carbon.  
 Third analysis gave 1.33 per cent. carbon.  
 Fourth analysis gave 1.29 per cent. carbon.

The thought occurred that perhaps the carbide obtained from molybdenum steel gives up part of its carbon as hydrocarbon on being brought into contact with the air during stirring. No heat was applied to hasten the solution at any time. A number of trial analyses were made in which the time of stirring was varied and also the acidity of the copper and potassium chloride solution.

In the following, 2 grams of the drillings were dissolved in 180 cc. of the double chloride solutions. By *acid* solution is meant a solution prepared by dissolving 600 grams of double chloride of copper and potassium in 1500 cc. of distilled water acidulated with 175 cc. of concentrated hydrochloric acid. By *nearly neutral* solution is meant the same as the acid solution except that but 25 cc. of concentrated hydrochloric acid were added to the 1500 cc. of distilled water.

The *neutral* solution consisted of 600 grams of the double chloride, 1500 cc. of distilled water and *no* acid. The results obtained are given in the following table:

STEEL CONTAINING 4 PER CENT. MOLYBDENUM AND 4 PER CENT. CHROMIUM.

Kind of steels.	Kind of solvent	Time of stirring. Minutes	Time in the solvent with no stirring. Hours.	Percentage of carbon found.
No. 1 steel	acid	20		1.53
No. 1 steel	"	20		1.48
No. 1 steel	"	10		1.64
No. 1 steel	"		12	1.49
No. 1 steel	"		24	1.52
No. 1 steel	nearly neutral	8		1.60
No. 1 steel	" "	8		1.55
No. 1 steel	acid	3		1.60
No. 1 steel	neutral	6		1.593
No. 1 steel	"	6		1.606
No. 2 steel	"	4		1.679
No. 2 steel	"	6		1.734
No. 2 steel	acid	4		1.758
No. 2 steel	"	4		1.66

A combustion of the 4 per cent. chromium, 4 per cent. molybdenum steel (No. 2), by the red lead process described below yielded 1.734 per cent. carbon.

An examination of the foregoing table shows that both in the No. 2 and the No. 1 steels the highest result was obtained when the acid solvent was used and also the lowest results.

Short stirring gave better agreements than the longer periods of stirring but had evidently not eliminated all of the causes of loss. Perhaps there is loss of carbon when the carbide is being dried in the water-oven. Further, it is practically impossible to regulate the suction so as to expose the residues, during washing, to exactly the same amount of air in each analysis.

Two grams of the No. 2 steel were stirred twenty minutes with

180 cc. of the acid solution, then transferred to the asbestos plug. Air was next drawn through the residue for fifty minutes; the amount of carbon obtained was 1.347 per cent. Two determinations of the same steel were made with sixty minutes' stirring but with the least possible exposure to suction; 1.63 per cent. and 1.68 per cent. carbon were found. In view of these results the practice was adopted of always keeping a layer of distilled water over the carbide during the washing. As soon as one layer, or covering of water, was drawn off, another was immediately supplied.

This treatment was applied to a group of ingots containing 11 per cent. of molybdenum and some chromium. The neutral solution gave the higher results as shown by the following table:

Acid solvent Per cent carbon.	Neutral carbon. Per cent. carbon.
0.52	0.60
0.46	0.56
0.53	0.59

The same process of short stirring and least possible exposure of the carbide residue to air by suction, together with the use of a neutral solvent, was adopted for a series of ingots containing 12 per cent. of molybdenum and several per cent. of chromium. It failed almost completely. For convenient comparison the results obtained in these latter experiments are shown in a column parallel to those obtained, at a later date, from the same samples by the red lead combustion method.

One well-known laboratory obtained 0.72 per cent. carbon and another, equally experienced, reported 0.64 per cent. carbon on the S. H. S. sample.

This untrustworthiness of the double chloride process for separating carbon in steel of high molybdenum and chromium content led to a search for some method of obtaining the percentage of carbon by burning the entire substance. Having about this time noted Brearley and Ibbotson's statement that steel drillings that will pass a 20-mesh sieve and have been mixed with about three times their weight of red lead can be decarbonized in a red hot porcelain tube, it was decided to attack the molybdenum steel in this manner. The results obtained from the molybdenum steels have been already given and need no comment.

Sample. 12 per cent. Mo. steel containing Cr.	Results obtained by the neutral solution. Per cent. carbon.	Results by the red lead process. Per cent. carbon.
No. 1 .....	{ 0.54	0.80
	{ 0.72	0.79
No. 2 .....	{ 0.81	
	{ 0.51	0.76
No. 3 .....	{ 0.66	
	{ 0.49	0.82
	{ 0.51	
No. 4 .....	{ 0.54	
	{ 0.58	0.81
"2nd trial" .....	{ 0.47	{ 0.88
	{ 0.61	{ 0.85
No. 5 .....	{ 0.61	{ 0.88
	{ 0.88	{ 0.87
No. 6 .....	0.49	0.73
S. H. S. ....	{ 0.69.88	
	{ 0.66	
	{ 0.68.75	
No. 7 .....	{ 0.66	0.94
	{ 0.52	0.939
No. 10. ....	{ 0.76	
	{ 0.75	1.00
	{ 0.62	
No. 11. ....	{ 0.72	0.80
	{ 0.52	

The method was first applied to plain carbon steels, pig iron, and white iron and was found to be perfectly accurate.

After more than eighteen months' daily use of the red lead for the determination of carbon in steel, pig iron, alloy steels and ferro alloys, the details that have been found useful and reliable are as follows:

If the borings are coarse, the thin curly portions of not over 1 mm. thickness are selected. It is rarely necessary to operate with even this thickness. Not more than 2 grams of such drillings and not less than 4 grams of the red lead are weighed into a glass-stoppered 60 cc. weighing-bottle. The bottle is then shaken to mix the drillings and lead oxide.

The steel sample submitted for analysis is drilled with a flat or diamond pointed drill. This style of drill will grind many of the drillings to 20-mesh fineness in the case of soft or annealed steels. If the steel be unannealed and of a carbon content ranging from about 0.35 per cent. carbon and higher, thin curly drillings are obtained which decarbonize readily by reason of thinness.

Care is taken at all times to cover such bulky drillings with the oxide of lead as any drillings that project above the main body of the charge are likely to escape oxidation.

For soft steels and annealed steels two sieves are used. One has a 20-mesh gauze and the other one a 30-mesh gauze. Those drillings that pass the 20-mesh gauze but do not pass the 30-mesh sieve are used for analysis.

This arrangement rejects the fine dust and the thick drillings. When very small pieces of steel are received they are drilled with  $\frac{3}{16}$  inch diameter twist or straight drills. All sizes of the flat, or diamond point drills are kept at hand from  $\frac{1}{4}$  inch diameter to  $\frac{7}{8}$  inch. Any good mill blacksmith can make the flat drills. By these means it is rarely, if ever, necessary to resort to the copper and potassium chloride separation of the carbon. In the laboratory of the Park Steel Co., where from twenty-five to thirty-five combustions are made each day, covering a range from 0.04 to 3.5 per cent. carbon, the writer does not recall a single instance in a year's time when it was necessary to resort to the double chloride process.

The mixture of lead oxide and drillings is transferred from the weighing-bottle to porcelain boats. The Royal Meissen brand  $15 \times 75$  mm. or  $112 \times 12$  mm. is mostly used, being convenient sizes. The porcelain boats are slipped into porcelain tubes of 16 mm. inside diameter  $\times 600$  mm. long. Two furnaces with their porcelain tubes are operated at the same time. Until recently, the outlet ends of these tubes were filled for a distance of 125 mm. with granulated copper oxide. Later the copper oxide was found to be unnecessary. Oxygen is used during the combustion. It passes through a preheating furnace filled with 125 mm. of copper oxide, then through a jar containing pieces of caustic potash (Fig. 3). It next bubbles through a solution of potassium hydroxide contained in a safety apparatus (Fig. 1) and is then dried in jars of soda-lime and calcium chloride of the design given in Fig. 3. This drying and purifying apparatus can be readily arranged and securely fastened in a space  $250 \times 406$  mm.

The combustions are operated in the usual manner. The portion of the tube containing the copper oxide is heated to redness, and then the remainder of the tube lying within the furnace is brought to the same temperature. The combustion tubes are constantly



kept hot through half the length so that the combustion commences almost as soon as the stoppers are inserted. While the boats are being charged the oxygen is passing slowly through the

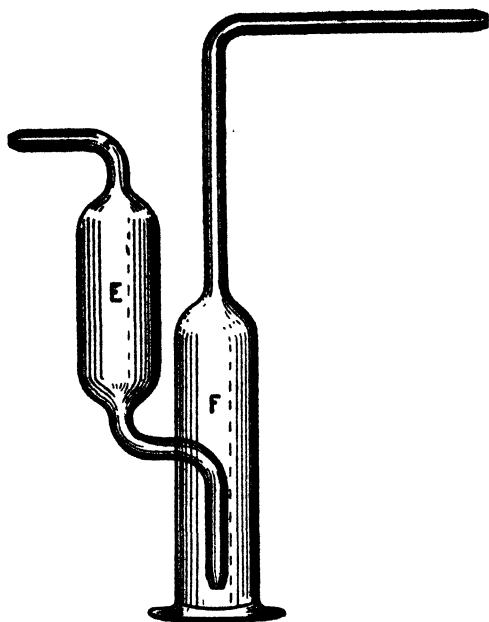


Fig. 1.

tubes and the weighing and absorbing apparatus which has been previously weighed and attached. (This weighing apparatus is shown in Fig. 2. It was designed by the writer as a substitute for the different forms of potash bulbs now in the market. It is made of heavy glass. It is easily kept clean, is not top-heavy, and does not occupy much space in a balance case.) As soon as the steel begins to burn there is, at first, a rapid evolution of gas which quickly ceases. More oxygen is then turned into the apparatus from the steel cylinder so that a very slow bubbling is maintained through the weighing apparatus. When the oxidation of the charge is completed, the oxygen begins to rush through the apparatus at a high rate of speed. The flow of the gas is quickly checked to a normal rate, that is, it is checked so that, as it leaves the preheater, it passes through the safety apparatus (Fig. 1) at a rate of about 26 bubbles per ten seconds. The stream is evenly distributed to the two combustion tubes by means of a Y-tube and screw pinch-cocks. The stream passes

through the weighing apparatus (Fig. 2) at the rate of 250 cc. every ten minutes which is the normal speed. When the com-

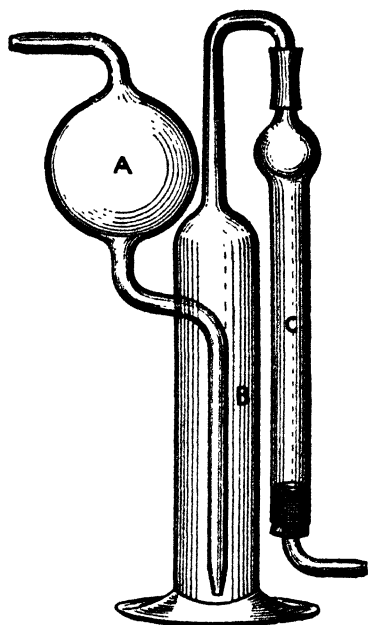


Fig. 2.

bustions are completed in both sets of apparatus, as indicated by the passage of the gas at a high rate of speed, the normal is then maintained through the red hot tubes ten minutes longer to insure complete oxidation and that all of the carbon dioxide has been carried to the weighing apparatus. The products of the combustion pass through a purifying train shown in Fig. 4. The train connects with the glass tube leading from the outlet end of the porcelain combustion tube, by means of heavy combustion rubber tubing, at H. The gases pass through the cylinder (I) which contains a column of granulated zinc of 20-mesh fineness. The use of granulated zinc to remove acid and chlorine in carbon combustions was first suggested by Dr. Edward S. Johnson. Cylinder I is  $254 \times 13$  mm. The zinc is held in place with plugs of glass wool. The gases next enter a cylinder (J) which contains a column of phosphoric anhydride. The phosphoric anhydride powder is held in place with plugs of ignited asbestos. Cylinder J is  $178 \times 13$  mm. Glass wool plugs should

not be used in J as they become clogged after a few combustions. Ignited asbestos is free from this objection.

The carbon dioxide, which is now freed from litharge and any acid fumes by zinc and from any moisture by the phosphoric anhydride, enters the weighing apparatus (L). This weighing

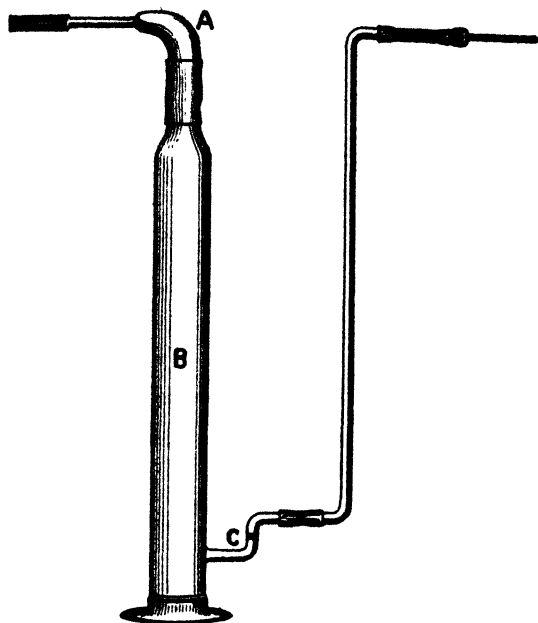


Fig. 3.

apparatus, as shown in the complete train (Fig. 4), differs slightly from the writer's first design shown in Fig. 2. The apparatus is charged with 20 cc. of potassium hydroxide consisting of one part of caustic potash dissolved in two parts of water. The drying tube (C) is filled with small pieces of *dry* caustic potash obtained by quickly cracking dry sticks of caustic potash in a porcelain mortar. Each end of the drying tube (C) contains a plug of asbestos or glass wool. Before inserting the rubber stopper in C care must be taken to free the surface of the tube (C) from any moist caustic potash as potassium hydroxide causes decomposition of rubber, resulting in continuous loss of weight.

The weighing apparatus is ready for recharging at the end of the fortieth combustion. The tare is then used for the absorbing and weighing of the carbon dioxide obtained from the next forty combustions, the exhausted apparatus now constituting the tare.

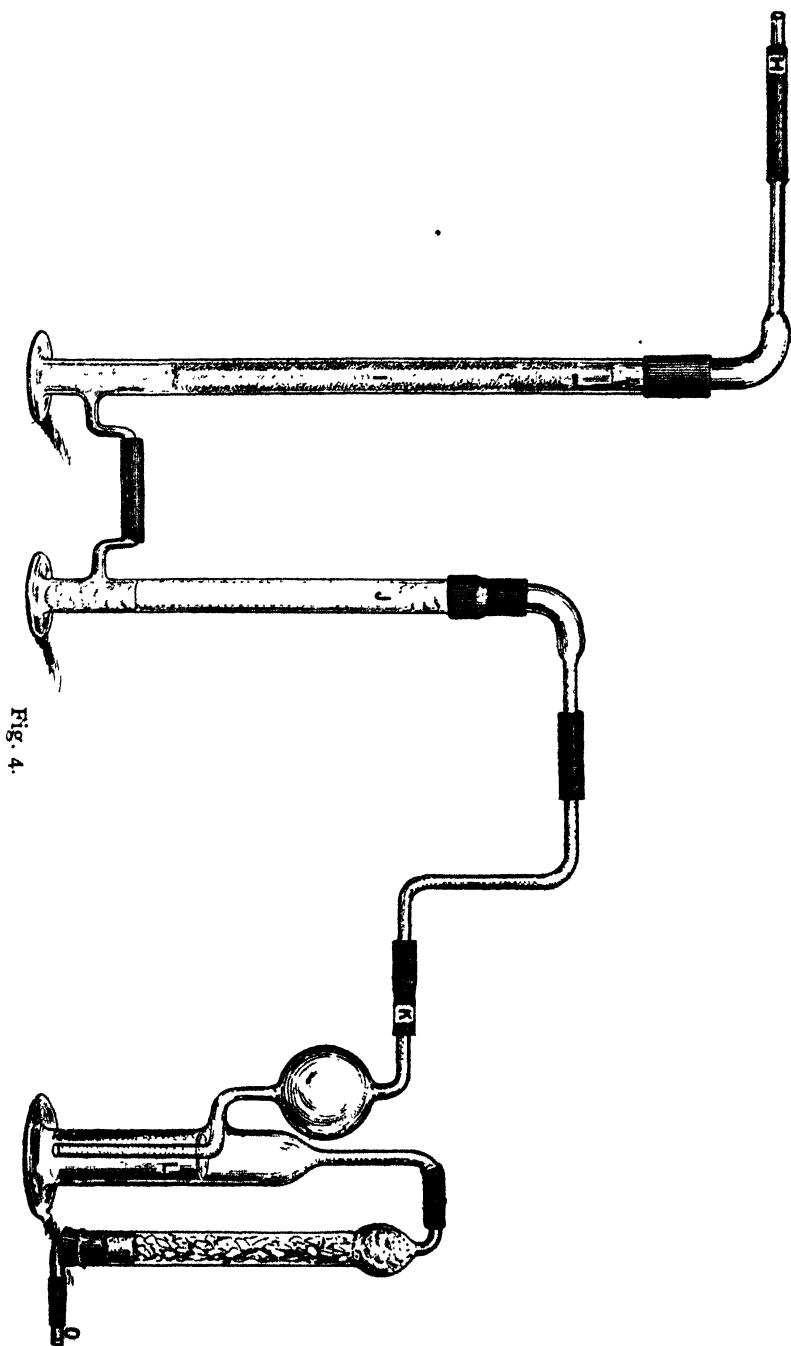


Fig. 4.

During the passage of the oxygen and the subsequent aspiration of the weighing apparatus to remove any oxygen present, the outlet, (O) Fig. 4, is protected from the ingress of moisture or impure air by a guard tube filled with small pieces of caustic potash. This guard tube is not shown in Fig. 4. All parts of the apparatus shown in Fig. 4 are connected by heavy-wall pure rubber tubing.

When the combustions are completed the weighing apparatus is detached from its train and the outlet of the train is closed with a glass plug. The weighing apparatus from each train is then connected to a tower, of the style shown in Fig. 3, which is filled with small pieces of caustic potash. Air is then drawn through this tower into the weighing apparatus for ten minutes to remove oxygen. The apparatus and its tare are next carefully wiped with a clean linen handkerchief and are placed in the balance case for weighing. The inlet and outlet of the weighing apparatus are kept closed with rubber caps except during weighings or when attached in the train (Fig. 4).

The method of using an exact duplicate of the weighing apparatus for a tare exposes the same amount of surface to the air during weighings and avoids the use of the larger weights.

Single combustions by this process have been made in this laboratory in fifty-five minutes.

As previously stated the porcelain tubes are kept red hot throughout one-half their length night and day so that the combustion commences in a minute or two after the boat is inserted and the combustion tube is stoppered. The remaining burners are lighted immediately after the tube is closed.

The red lead used in this work must be thoroughly mixed and ground free of lumps before its carbon content is determined. The so-called pure red lead costing about 9 cents per pound in fifty-pound lots is found satisfactory for the purpose. Blank combustions with 4 grams of red lead are at present yielding 6 mg. of carbon dioxide which are deducted from each determination. Blank combustions or analyses of standard steels should be made each day. The red lead is kept in tightly stoppered bottles.

The method of weighing the carbon dioxide obtained in the red lead combustions as barium carbonate was tried for several months. As it is not necessary to dry the carbon dioxide in this

modification of the red lead method, the carbon dioxide was passed through a cylinder illustrated by Fig. 3 filled with granulated zinc to remove litharge fumes, and from thence the carbon dioxide entered the absorbing apparatus which consisted of two  $254 \times 25.4$  mm. test-tubes connected in tandem and containing barium hydroxide solution. The solution in the first tube converts the bulk of the carbon dioxide formed into barium carbonate but in the higher carbon steels a little escapes into the second tube.

The barium carbonate is filtered through 12-cm. filters reinforced at the apex by a piece of cheese-cloth. The precipitate is washed thirty times with distilled water, allowing each washing to be drawn off by slight suction.

The cheese-cloth is removed and the precipitate is ignited and weighed. From this weight the amount of barium carbonate formed from the impurities in the red lead and that obtained from the unavoidable exposure of the excess of the hydroxide during filtration and washing is deducted. From the net weight of barium carbonate the percentage is calculated.

The barium hydroxide solutions are prepared by dissolving, or nearly dissolving, 200 grams of barium hydroxide crystals in four liters of water. It is filtered by suction through a paper pulp filter and preserved with the usual precautions. The test-tubes for the solution are provided with 30 cc. and 70 cc. marks. The pair of tubes constituting the absorption pair are filled to the 30 cc. marks with water and the barium hydroxide solution is then poured in until the 70 cc. marks are reached.

A protracted comparison of the two gravimetric processes described in this paper extending over a period of several months was made. The method whereby the resultant carbon dioxide was weighed as barium carbonate checked excellently with the one in which the carbon dioxide was absorbed and weighed in the apparatus shown in either Fig. 2 or in the termination of the train, Fig. 4, agreeing within 0.01 per cent. or less. The latter process is preferred as requiring less manipulation, less oxygen, and less time. In the barium carbonate method it was necessary to force the oxygen through the safety apparatus (Fig. 1) at the rate of 38 bubbles per ten seconds on account of the resistance to the passage of the gas through the absorption test-tubes.

The ordinary ten-burner Bunsen combustion furnace is employed but with certain alterations to secure higher heating power. At the points where the porcelain tubes rest in the ends of the furnace these ends are slotted down about 25 mm. This permits the tubes to lie well enveloped with the flames. Further, under each foot of the furnaces pieces of fire-brick about 28 mm. thick are placed. Also the rows of burners are lowered until they rest on the laboratory table. To keep the rows vertical one burner at each end of the rows is wired to the furnace. This lowering of the burners and raising of the furnace frame, by use of the fire-brick, improves the draught and secures hot flames with a minimum gas pressure. Clay gutters are placed under the porcelain tubes to prevent sudden cooling. Strips of wet blotting-paper about 25 mm. wide are wrapped around the ends of the porcelain tubes to keep the rubber stoppers from burning. The ends of these strips dip into suitable vessels of water.

Porcelain tubes glazed inside only, of 16 mm. inside diameter by 600 mm. long, will last from six weeks to two months when in use night and day. Flames are always kept under the tubes. Such tubes cost about \$1.80 each.

Porcelain boats are cleaned for further use by allowing them to stand in nitric acid of 1.20 sp. gr. for some hours. The boats are ignited a few minutes in the flame of a Bunsen burner just before being used. Porcelain boats 14-15 mm. wide by 70-75 mm. long, Royal Meissen brand, are quoted in ten-gross lots at \$14.50 per gross. These boats can be used three times.

The apparatus shown in Fig. 1 was designed as a safety apparatus to prevent the potassium hydroxide solution from blowing over into the rubber tubing from any cause. The oxygen, as it leaves the preheating furnace, enters the chamber E and bubbles through chamber F which is filled to one-third its capacity with potassium hydroxide solution consisting of one part of caustic potash dissolved in two parts of water. F is 35 mm. outside diameter by 170 mm. long. Fig. 3 shows a tower or jar that is used as a container for small pieces of stick caustic potash for purifying the oxygen. The pieces of apparatus shown in Figs. 1, 3 and 4 were designed by the writer to avoid the use of rubber stoppers.

The following results attest the accuracy of the red lead process:

Name of sample.	Weight of sample taken. Grams.	Weight of lead oxide used. Grams.	Per cent. carbon by red lead.	Per cent. carbon by double chloride.
S. S. Co. carbon steel.....	3	9	0.395	0.415
No. 690.....			0.985	0.96
No. 350, tungsten steel.....			1.285	1.29
No. 353, tungsten steel.....			1.338	1.354
No. 22, high per cent. nickel steel...			0.698	0.696
No. 14, nickel steel .....			0.447	0.450
S XIX, high per cent. tungsten steel			{ 2.40	2.35
			{ 2.39	
Wash metal.....	1 $\frac{1}{2}$	1 $\frac{1}{2}$	{ 3.56	3.59
			{ 3.65	
Wash metal .....	1 $\frac{1}{2}$	3	3.58	
C. B. pig metal.....	1 $\frac{1}{2}$	$\frac{3}{4}$	4.01	
C. B. pig metal.....	1 $\frac{1}{2}$	1 $\frac{1}{2}$	4.04	4.04
Soft O. H. steel No. 1.....	6	3	0.192	0.185
Soft O. H. steel No. 2 .....	8	4	0.097	0.077
Soft O. H. steel No. 3761 .....	6	3	0.156	0.145

In July, 1901, a sample of steel was sent by Sanderson Bros. Steel Works to several laboratories. The writer retained a portion of these drillings for several years. The different laboratories reported as follows:

	Per cent. carbon.
Atha Steel Works obtained.....	1.25
Crescent Steel Works obtained.....	1.20
Park Steel Works obtained.....	1.214
Spaulding Jennings Steel Works obtained.....	1.199
Sanderson Bros.' Works obtained.....	1.214
La Belle Steel Co.'s Works obtained.....	1.20
3 grams of this sample plus 1.5 grams of red lead burned in stream of oxygen gave.....	1.22

In March, 1901, the following parties reported the carbon of another sample of steel:

	Per cent. carbon
Booth, Garret & Blair reported.....	1.277
Sanderson Bros. reported.....	1.292
Park Steel Co. reported.....	1.301
Bethlehem Steel Co. reported .....	1.307
Crescent Steel Co. reported.....	1.315
3 grams of this sample decarbonized with 1.5 grams of red lead yielded.....	1.305

The writer has since had occasion to compare results with other laboratories covering a range in carbon from 0.32 to 1.45 per cent. carbon with equally good agreements.



## CARBON IN FERRO-CHROMIUM.

In applying the red lead process to ferro-chromium, it was found that the maximum carbon in the 65 per cent. chromium alloy was obtained by burning the alloy with three to four times its weight of red lead.

Ferro-chrome.	Weight of sample taken. Gram.	Weight of red lead used. Grams.	Per cent. carbon found.
Sample A.....	1	2	7.26
" .....	1	3	7.54
" .....	1	4	7.72
" .....	$\frac{1}{2}$	3	7.73
Sample B.....	$\frac{1}{2}$	$2\frac{1}{2}$	7.03
" .....	$\frac{1}{2}$	4	7.00
Sample C.....	$\frac{1}{2}$	$2\frac{1}{2}$	6.46
" .....	$\frac{1}{2}$	$3\frac{1}{2}$	6.55
Sample D.....	1	1	6.05
" .....	$1\frac{1}{2}$	$\frac{3}{4}$	5.17
" .....	1	2	6.403
" .....	1	4	7.094
" .....	1	3	7.15
Sample E.....	1	4	7.07
" .....	$\frac{1}{2}$	4	7.18

In February, 1906, the copper oxide was omitted from one combustion tube. The space ordinarily occupied with copper oxide was filled, loosely, with ignited asbestos. The following results indicate that the use of copper oxide in combustions with red lead is unnecessary:

Sample.	With copper oxide. Per cent. carbon.	Without copper oxide Per cent. carbon.
3 sq. steel .....	1.479	1.477
No. 288 .....	1.175	1.175
6 S.....	0.207	0.207
No. 1193 .....	0.712	0.692
No. 7013 .....	0.520	0.538
C No. 2 .....	1.48	1.51
No. 2703 .....	0.316	0.309
No. 385 .....	0.425	0.439
No. 7014 .....	0.396	0.393
No. 7013 .....	0.401	0.397
No. 1241 .....	0.75	0.765
C No. 3 .....	1.281	1.283
No. 7015 .....	0.409	0.407
No. 7016 .....	0.481	0.478
No. 7017 .....	0.312	0.315
No. 7018 .....	0.425	0.43
No. 7020 .....	0.431	0.431
No. 1200 .....	0.73	0.75
Ferro-manganese .....	6.31	6.39
Mixture of plumbago and clay.....	45.96	46.04
Pig iron "B" .....	3.61	3.58

The omission of copper oxide would permit the use of shorter porcelain tubes and shorter combustion furnaces. A red hot body of copper oxide hastens breakage of porcelain tubes by causing unequal cooling strains when the furnace flames are lowered or extinguished for any reason. Since February one tube has been in use without copper oxide. The oxide is still retained in the companion tube so that daily comparisons have been made.

LABORATORY OF THE PARK STEEL WORKS,  
CRUCIBLE STEEL CO. OF AMERICA, PITTSBURG, PA.,  
April 26, 1906.

## THE NITROMETER.

BY J. NEWFIELD AND J. S. MARX.

Received February 12, 1906

HAVING occasion to use the nitrometer extensively in our work we have made a study of some of the factors which affect the results obtained by means of this instrument, especially with reference to its use in the analysis of nitrocellulose and other explosives. We have used the form known as Lunge's Improved Nitrometer or Gas Volumeter

A description of this apparatus is very well given in Sutton's "Volumetric Analysis," eighth edition, pages 616 to 618. It consists in brief of a decomposing bulb connected by a heavy rubber tube to an overflow. By means of a small piece of rubber tubing this bulb can be connected to a long measuring tube graduated to tenths of cubic centimeters. Temperature and barometric corrections are dispensed with by having a closed tube inserted between the measuring tube and its overflow, all three being joined together by means of a rubber tube. In this sealed tube are 100 cc. of air over mercury at 760 mm. pressure and 0° C. temperature. Thus when the volume of air in the tube is 100 cc. and the mercury column leveled with that in the measuring tube, its gas is also under the same conditions of temperature and pressure.

However, it would be difficult and also unnecessary to obtain just 100 cc. of air in the sealed tube under standard conditions, so a factor is obtained in the following way: Approximately 100 cc. of air are introduced into the sealed tube, then a weighed portion of perfectly pure, dry potassium nitrate is run through the apparatus. From its composition 1 gram of the nitrate gives 221 cc. of nitric oxide gas, under normal conditions. The differ-

ence between 221 cc. and what is actually obtained by experiment "fixes" the factor which is used in all subsequent determinations. About 40 to 50 cc. of sulphuric acid are used in making a determination.

EFFECT OF SULPHURIC ACID OF DIFFERENT CONCENTRATIONS.

Strength of acid. Per cent.	Cubic centimeters of NO per gram $\text{KNO}_3$ .
97.18	221.11
96.59	221.08
94.81	221.09
94.05	221.10
93.02	221.60
90.96	223.43
85.20	223.61

As the original factor is fixed by the use of potassium nitrate, these results only indicate that changes in the concentration of the acid between 97 and 94 per cent. are without effect, but a weaker acid gives too high results, probably because it absorbs less of the nitric oxide. That the stronger acid absorbs nitric oxide was shown by the following experiments: On agitating 112 cc. of nitric oxide with 40 cc. of sulphuric acid of 97 per cent. for three minutes 1 cc. or 0.89 per cent. was absorbed. On shaking 112 cc. with 40 cc. of an acid of 85 per cent. 0.5 cc. or 0.45 per cent. was absorbed.

Determinations made with acid from 85 to 50 per cent. gave widely varying results, indicating that reliable values can not be obtained with such weak acids.

In the analysis of nitrocellulose and similar explosives the strength of the acid is even more important, as will be seen from the following table:

Strength of acid Per cent.	Cubic centimeters of nitric oxide per gram cellulose.
97.18	199.5
96.59	199.5
94.81	199.7
94.05	197.1
93.02	193.1
88.60	147.5

Here it is evident that an acid weaker than 94.8 per cent. does not effect a complete decomposition of the nitrocellulose, probably because the weaker acids do not completely dissolve the gun-cotton.

*Effect of Temperature.*—Between  $15^\circ$  and  $40^\circ$  the temperature

at which the decomposition is effected is without appreciable effect on the results obtained either with potassium nitrate or with nitrocellulose. At  $40^{\circ}$  or above, loss of nitric acid or oxides of nitrogen occurred on the addition of the sulphuric acid, causing low results.

*Effect of Time of Agitation.*—The following results were obtained with acid of 97 per cent. at  $15^{\circ}$ :

Time of agitation Minutes.	Cubic centimeters of NO per gram $\text{KNO}_3$ .	Cubic centimeters of NO per gram nitrocellulose.
1	221.07	200.8
2	220.89	.....
3	220.98	201.9
5	220.97	201.8
8	220.92	201.8

It seems that a complete decomposition of the potassium nitrate is secured in one minute, while three minutes should be used for nitrocellulose.

*Effect of Pressure.*—The following results were obtained with acid of 97 per cent. at  $15^{\circ}\text{C}$ , the pressure being roughly calculated from the difference in heights of the mercury columns in the decomposing and overflow bulbs.

Pressure (pounds per square inch)	Cubic centimeters of NO gas per gram $\text{KNO}_3$ .
7	221.73
14 (normal)	221.03
30	219.95

It is seen from the above that the pressure at which the gas exists exerts a marked effect on the results obtained. This is explained by the fact that the higher the pressure exerted on the gas, the more nitric oxide is dissolved in the sulphuric acid. Always keeping the gas at a slightly reduced pressure appears to give very satisfactory and accurate results.

*Effect of Standing Dissolved in Sulphuric Acid.*—Experiments were carried on with the aim in view of determining if there is any marked difference in results to be noted when organic nitrogenous bodies are allowed to remain for some time in sulphuric acid before decomposing in the nitrometer instead of immediately decomposing as is the method employed here. The results follow. As will be noticed, some of the samples were allowed to stand in ice over night to prevent any possible local heating, but the results do not vary much from those which were simply allowed to stand over night under ordinary conditions.

	First method. Decomposing immediately.	Second method. Standing for twelve hours. before decomposing.	
		In ice.	Not in ice.
	198.1	202.8	202
Same guncotton...	198.3	201.6	201.6
	198.0	202.3	202.6
		203.8	203.7
	201		208.2
			205.3
	201		204.3
			203
	202		205
			204
	200		205 (in desiccator)
	192.3		196.4
			194.7
	200		205.3

With a view of determining the cause of the above difference, a sample of guncotton weighing 0.6 gram and analyzed in the ordinary way (*i. e.*, first method) read 119.7 cc. on the nitrometer. The gas was run into strong commercial caustic potash solution and after saturation the loss of gas was found to be only 0.7 cc.

Then into this caustic potash solution, saturated with nitric oxide, was run the gas obtained from one of the guncottons which had been analyzed by the second method and the result was as follows:

First method.	Second method.	After absorption.
200	205.3	196.9

Several checks were made on the above with similar results.

We know that it is impossible for most of the results obtained by the second method to be correct, for extended researches have shown that guncotton having a nitration of 204 cc. and upwards is not soluble in a mixture of two parts ether and one part alcohol and yet all these guncottons tested were practically entirely soluble.

*Effect of Other Organic Substances.*—The following experiments show the effect of the presence of various organic bodies and other substances (many of which occur in dynamites and gelatines) on the determination of nitrogen by the nitrometer.

In every case a weighed portion of potassium nitrate (about 0.55 gram) was taken, and from 0.05 to 0.1 gram of substance was

added. The mixture was allowed to stand over night in sulphuric acid and was then run through the nitrometer. Of course, in this case standing over night does not affect the result as there is no organic matter present which can be decomposed and the small amount of nitric oxide gas lost is constant in all determinations, including those in which the factors were determined.

Results are tabulated as follows:

No.	Substance.	Amount taken. Gram.	Result in cc.	Result with chromic acid.	Result after absorption with KOH.
1	Resin	0.1	212.4		
2	"	0.1		219.1	214.9
3	Camphor	0.1	203.4		
4	"	0.1		219.4	199.8
5	Sulphur	0.1	225.3		
6	"	0.15	227.3		
7	Paraffin	0.1	199.5		
8	"	0.05	209.5		
9	Vaseline	0.2	217.6		
10	"	0.05	218.7		
11	MgCO <sub>3</sub>	0.05	223.4		
12			221.0		

The following can be deduced from the results. All the organic compounds, as in 1, 3, 7 and 9, affect the results in such a way as to give low values. Paraffin has the greatest effect, then camphor, then resin, then vaseline. The effect of adding chromic acid, as seen by the absorption results of potassium hydroxide, is to oxidize some of the carbon to carbon dioxide and thus raise the results, but practically no more nitric oxide is obtained by this treatment. In the table, 2 and 4 show this.

The two inorganic substances used, sulphur and magnesium carbonate, on the contrary, tend to make the result a little high. This is explained in the first case by the formation of a little sulphur dioxide and in the second case by the formation of a little carbon dioxide which is retained by the sulphuric acid and expelled during the violent shaking in the decomposing bulb. This latter is similar to the cases already cited where carbon dioxide is formed when organic nitrogenous compounds are allowed to remain over night in the sulphuric acid before decomposing in the nitrometer.

In summing up the above results we can at once see that the nitrometer is a very delicate instrument, by which, when all

standard conditions are adhered to, very accurate results may be quickly obtained.

The scope of its usefulness, however, is somewhat limited and a great number of details, apparently trivial, affect the results to a considerable extent.

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## THE DETERMINATION OF SILICA IN IRON ORES CONTAINING ALUMINA.

BY GRAHAM DEAN.

Received April 18, 1906.

I HAVE found that if the insoluble residue left on the treatment of an iron ore with acids is ignited for a short time the aluminum which it contains is converted into a form which dissolves in concentrated hydrochloric acid. On the basis of this fact the following rapid method for the determination of silica in such ores has been developed.

One gram of the finely powdered ore is dissolved on the hot plate in concentrated hydrochloric acid, using an initial amount of 25 cc. Boil until the iron is completely dissolved, adding two or three drops of nitric acid near the end. If pyrites is present, more nitric acid may be required. Nearly all iron ores will yield to this treatment; if an ore does not, the results are worthless.

Evaporate the solution to dryness, take up the residue with a small amount of concentrated hydrochloric acid, boiling till the ferric chloride is all dissolved. Dilute slightly, filter and wash thoroughly with hot hydrochloric acid (1:1). If a determination of alumina is required, this filtrate must be examined as well as the solution obtained below

Transfer the moist filter and residue to a platinum crucible and burn the filter carefully, as usual. Then set the crucible upright, put on the cover and ignite for two or three minutes over a Dangler burner. I have found that the proper temperature is best secured in a dull or carbon covered platinum crucible. The ignition must not be continued too long and the temperature must be properly regulated.<sup>1</sup> I have repeatedly attempted to

<sup>1</sup> Dr. Hillebrand explains the results obtained by Mr. Dean by calling attention to the fact that the aluminum of kaolin is rendered soluble in hydrochloric acid by gentle ignition. See McNeil: *This Journal*, 28, 592. If the ignition is too intense, the aluminum becomes insoluble again. If this explanation is correct, the method would not be reliable for ores containing other silicates than kaolin.—EDITOR.

obtain good figures by use of bright and shining platinum crucibles but have never been able to do so.

When cold the contents of the crucible are transferred to a beaker, the cake pulverized with a glass rod and digested for seven or eight minutes with boiling concentrated hydrochloric acid.<sup>1</sup> The residue should feel soft and mushy under pressure unless the silica of the ore existed as free sand. Dilute slightly, filter and wash thoroughly. The filtrate may be combined with the first filtrate for the determination of aluminum. The residue, after ignition, may be considered as practically pure silica.

The precipitation of the alumina by phenylhydrazine,<sup>2</sup> I have found most satisfactory.

The figures given below are an average set selected from a large number of experimental determinations made with Mesabi ores containing in some instances a high percentage of alumina, a large portion of which was proved to be retained in the residue previous to separation and extraction. The results under the heading "Ignition" were obtained by the method given above.

	Ignition.	Sodium carbonate. fusion.	Hydrofluoric acid.
1.....	12.86	12.83	12.94
2.....	22.96	22.82	22.99
3.....	17.50	17.40	17.56
4.....	5.16	5.00	5.10
5.....	6.05	6.00	5.99
6.....	13.89	13.80	13.70
7.....	9.84	9.92	10.06

The following amounts of alumina were found in residues obtained by the new method: 0.06, 0.04, 0.10, 0.11, 0.02, 0.07, 0.05, 0.09 and 0.10 per cent. Before the separation by ignition and treatment with hydrochloric acid the residues retained from 4.25 to 10 per cent. of alumina. It is evident that the separation is sufficiently complete for technical purposes.

OLIVER IRON MINING CO.,  
HIBBING, MINN.

<sup>1</sup> One-fourth gram of potassium chlorate added at this stage will give slightly higher alumina results, which are also more concordant with fusion alumina. No time is lost, since the seven or eight minutes allotted will suffice to remove chlorine from the solution as well as alumina from residue.

<sup>2</sup> Campbell and Hess: This Journal, 21, 776. E. T. Allen: Ibid., 25, 423.

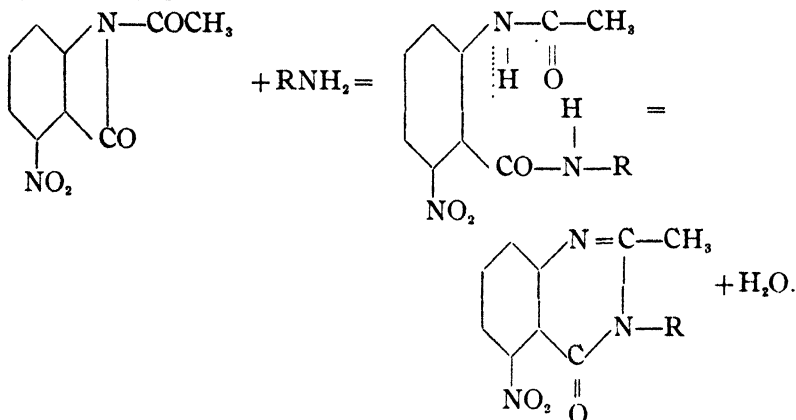


RESEARCHES ON QUINAZOLINES (FIFTEENTH PAPER<sup>1</sup>).  
ON A 3-AMINOQUINAZOLINE, AND THE COR-  
RESPONDING 3,3'-DIQUINAZOLYL, FROM  
6-NITROACETANTHRANIL AND  
HYDRAZINE HYDRATE.<sup>2</sup>

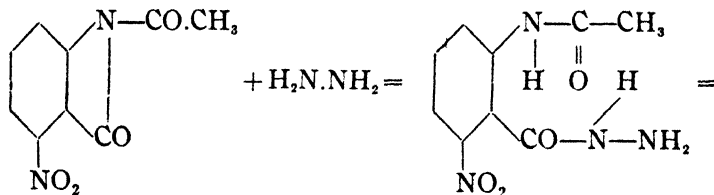
BY MARSTON TAYLOR BOGERT AND HARVEY AMBROSE SEIL

Received May 5, 1906

THE preparation of quinazolines from 6-nitroacetanthranil and primary monamines has been reported from this laboratory in previous papers,<sup>3</sup> the reactions involved being as follows:



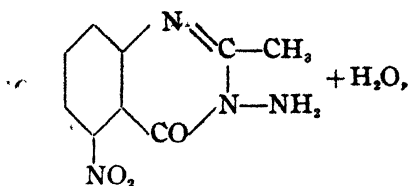
From an examination of these reactions it will appear that a similar condensation should occur with hydrazine, giving rise to aminoquinazolines and diquinazolyls:



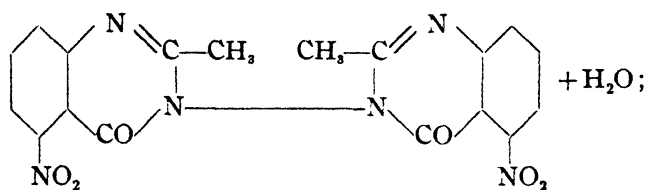
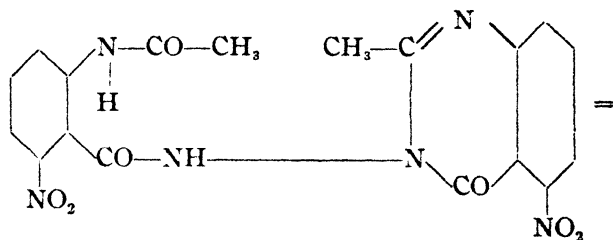
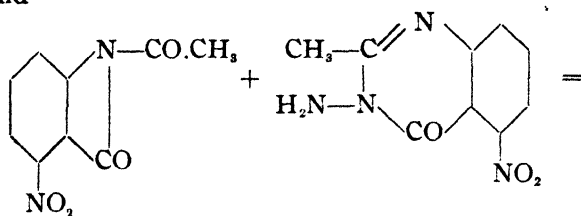
<sup>1</sup> The previous papers have appeared in this Journal, under various headings as follows: 22, 129, 522 (1900); 23, 611 (1901); 24, 1031 (1902); 25, 372, 935 (1903); 27, 649, 1127, 1293, 1302, 1305, 1327 (1905); 28, 94, 207 (1906).

<sup>2</sup> Read at the meeting of the New York Section of the American Chemical Society, April 6, 1906.

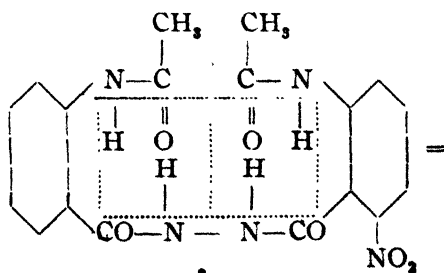
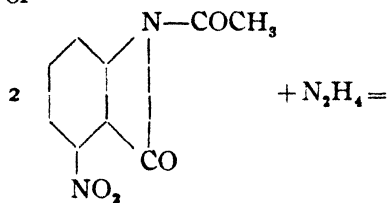
<sup>3</sup> Bogert and Chambers: This Journal, 27, 649; Bogert and Seil: Ibid., 27, 1305 (1905).

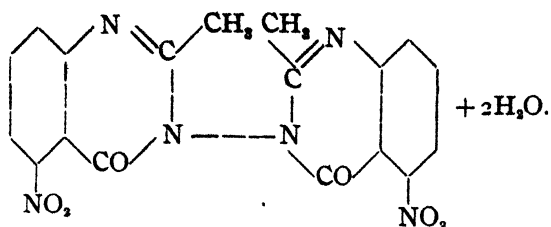


and



or





On testing this experimentally, such was found to be the case, as both the aminoquinazoline and the diquinazolyl were obtained.

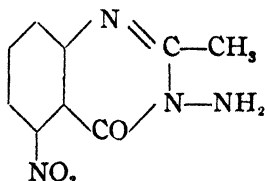
When equal molecules of the anthranil and hydrazine were used, the former being added gradually to the latter, the aminoquinazoline was the chief product. With two molecules of the anthranil to one of the hydrazine, adding the latter gradually to the former, the chief product was the diquinazolyl. The diquinazolyl was also produced by condensing the aminoquinazoline with a second molecule of the anthranil, but the yield by this method was poor.

The aminoquinazoline is easily separated from the diquinazolyl by its solubility in dilute alcohol. Its hydrochloride, chlorplatinate, diacetyl derivative, bromdiacetyl derivative, phenylhydrazinophenylhydrazone and uramino derivative were prepared and studied, as well as its behavior with potassium hydroxide, with chloroform and potassium hydroxide, and with benzaldehyde. The action of nitrous acid upon it is now being investigated, and the results will be reported later.

The diquinazolyl is difficultly soluble in most of the ordinary solvents, is not easily attacked by either acid or alkali, and forms no bromine derivative. With excess of acetic anhydride, addition apparently occurs on one nucleus only.

#### EXPERIMENTAL.

##### *2-Methyl-3-amino-5-nitro-4-ketodihydroquinazoline,*



—This was prepared by adding 6-nitroacetanthranil to the calculated quantity of hydrazine hydrate in 33 per cent. aqueous

solution. Reaction took place immediately, as was shown by the heat developed and the change in color from yellow to white. After boiling for a few minutes, to convert any amide to quinazoline, the solution was evaporated almost to dryness and filtered. The crude aminoquinazoline, yellow in color, was washed with dilute acetic acid, to remove any excess of base, and then extracted several times with water and finally with a mixture of alcohol and water. In this way it was separated from the diquinazolyl present. On evaporating the combined extracts to small bulk and allowing the solution to stand, beautiful, long, pink prisms of the aminoquinazoline were obtained, which, when treated with bone-black and recrystallized from dilute alcohol, appeared in long, colorless prisms. The aminoquinazoline is moderately soluble in water, alcohol or acetone; slightly soluble in chloroform or benzene; and almost insoluble in ether. It melts at  $152-153^{\circ}$  (corr.).

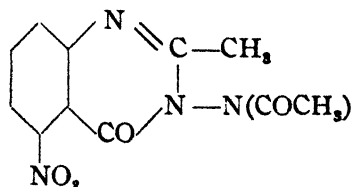
Calculated for  $C_9H_8O_3N_4$ : C, 49.09; H, 3.63; N, 25.45. Found: C, 48.91 and 48.86; H, 3.60 and 3.51; N, 25.46 and 25.43.

*Hydrochloride*.—Hydrochloric acid was added to a saturated aqueous solution of the aminoquinazoline. Small crystals separated at once, which gradually grew into flat, glistening plates.

The hydrochloride is insoluble in water, but soluble in dilute hydrochloric acid, from which it can be recrystallized. It is not hydrolyzed by boiling water, and melts at  $253-254^{\circ}$  (corr.).

*Chlorplatinate*.—The aminoquinazoline forms a chlorplatinate when chlorplatinic acid is added to an alcoholic solution acid with hydrochloric acid. Some reduction always occurs, and the yellow crystals of the chlorplatinate are thereby contaminated with metallic platinum. A pure sample for analysis could not be prepared.

*2-Methyl-3-diacetyl-amino-5-nitro-4-ketodihydroquinazoline*,



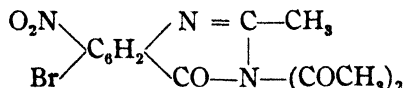
—The aminoquinazoline was dissolved in an excess of acetic anhydride, solution taking place gradually. The excess of anhydride was evaporated and the residual heavy syrup allowed

to crystallize. It was then dissolved in alcohol and allowed to cool slowly. Long, fine, white needles separated, melting at  $233^{\circ}$  (corr.).

The diacetyl derivative is insoluble in water, moderately soluble in hot alcohol, but practically insoluble in cold alcohol.

Calculated for  $C_{13}H_{12}O_8N_4$ : N, 18.42. Found: N, 18.74.

*Brom-2-methyl-3-diacetylamino-5-nitro-4-ketodihydroquinazoline,*

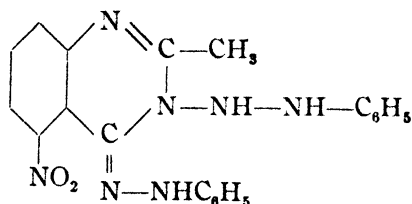


—Attempts to brominate the aminoquinazoline in aqueous solution gave negative results. A dark brown gummy mass was obtained, from which no pure substance could be isolated. Bromination of the diacetyl derivative, however, proceeded smoothly.

The aminoquinazoline was dissolved in acetic anhydride, and bromine dissolved in acetic anhydride was added to the warm solution until on gentle warming the color was no longer discharged. The bromine derivative precipitated as a white compact powder. The solution was allowed to cool, the precipitate filtered out and crystallized from dilute alcohol. Small yellow crystals resulted, which softened at  $105^{\circ}$  and melted at  $110^{\circ}$  (corr.).

Calculated for  $C_{13}H_{11}O_5N_4\text{Br}$ : N, 14.62; Br, 20.88. Found: N, 14.93; Br, 20.60.

*Phenylhydrazone of 2-methyl-3-phenylhydrazino-5-nitro-4-ketodihydroquinazoline,*



—This derivative was prepared by two methods: (1) by boiling the aminoquinazoline directly with phenylhydrazine; and (2) by dissolving the aminoquinazoline in acetic acid, adding an acetic acid solution of phenylhydrazine, and boiling the solution for an hour.

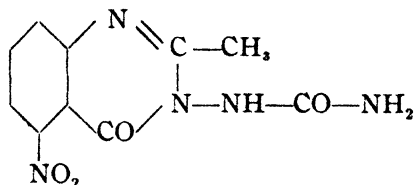
(1) The aminoquinazoline was warmed gently with an excess of phenylhydrazine. When boiling commenced the flame was

removed, the heat of reaction sufficing to maintain the boiling for several minutes. The reaction was completed by a further boiling over the flame for a few minutes. Ammonia was evolved during the reaction. The solution was acidified with dilute acetic acid, evaporated to small bulk, the residue taken up with alcohol, and the solution treated with bone-black. On standing, large, white, lustrous plates separated, melting at  $124-125^{\circ}$  (corr.).

(2) The aminoquinazoline was dissolved in acetic acid, alcohol and an excess of phenylhydrazine in acetic acid were poured in, and the mixture heated on the water-bath for an hour. Sufficient alcohol was added to yield a clear solution, and the whole set aside to crystallize. The crystals which separated corresponded entirely with those obtained by the first process.

Calculated for  $C_{21}H_{18}O_2N_7$ : N, 24.43. Found: N, 24.75.

*2-Methyl-3-uramino-5-nitro-4-ketodihydroquinazoline,*



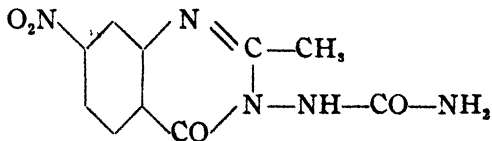
—An acid solution of the aminoquinazoline was treated with potassium cyanate, but no reaction occurred, and the aminoquinazoline was recovered unaltered.

The uramino compound was obtained, however, by condensing the nitroacetanthranil with semicarbazide, the reaction being entirely analogous to that between hydrazine and the acetanthranil by which the aminoquinazoline is formed. The crude product melted at  $263-264^{\circ}$  (uncorr.).

Calculated for  $C_{19}H_{14}O_4N_5$ : N, 26.61. Found: N, 26.48.

Not enough of the material was prepared to purify it further, as we were running short of our 5-nitroacetanthranil. The experiment, was therefore, continued with 4-nitroacetanthranil.

*2-Methyl-3-uramino-7-nitro-4-ketodihydroquinazoline,*



—Like the 5-nitro compound, the 7-nitro-3-amino-2-methyl-4-ketodihydroquinazoline (this compound will be described more fully in a subsequent paper) gave no uramino derivative when treated in acid solution with potassium cyanate, the aminoquinazoline being recovered unaltered.

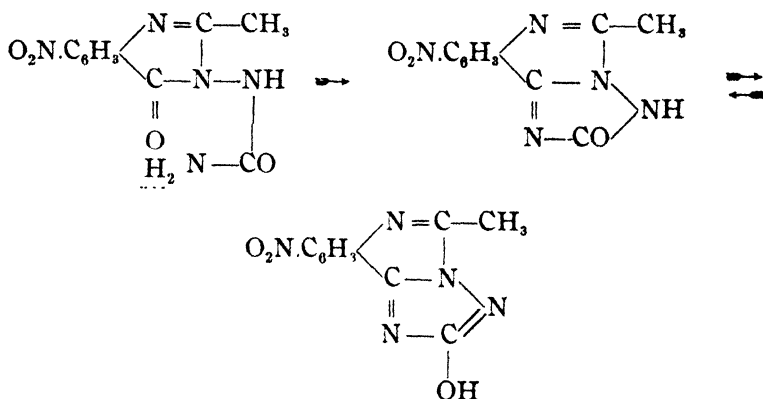
The 4-nitroacetantranil was then treated with an aqueous solution of semicarbazide in slight excess. At first no change was noted, but on heating vigorous reaction commenced and the whole mass finally solidified. After removing the water by filtration, the residue was washed with dilute acetic acid and crystallized from boiling water. Masses of fine, white, silky crystals separated in clusters, melting at  $266^{\circ}$  (corr.).

Calculated for  $C_{10}H_9O_4N_6$ : N, 26.61. Found: N, 26.24.

An aqueous solution of the substance gave a white flocculent precipitate when treated with bromine water.

The condensation of the nitroaminoquinazolines with thiosemicarbazide gave dark colored products, from which we were unable to separate any pure substance.

By the condensation of the uramino side chain in the above compounds with the adjacent keto group, a new triazine ring should be formed:



So far, our efforts to accomplish this condensation have been futile. The uramino compound was boiled with 20 per cent. hydrochloric acid, with phosphorus oxychloride (alone, and in nitrobenzene solution), with a mixture of phosphorus oxychloride and pentachloride, and with acetic anhydride in excess. Long boiling with the hydrochloric acid ruptured the triazine cycle, and hydrolyzed the compound completely to the nitroanthranilic

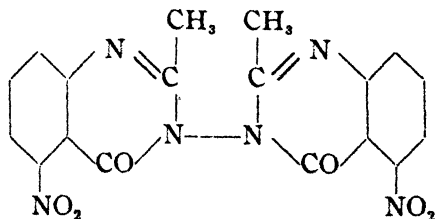
acid. The results of boiling with the phosphorus halides were likewise disappointing, charring taking place in every case. When the uramino-7-nitro compound was boiled with excess of acetic anhydride for half an hour, solution occurred slowly. When a clear solution was obtained, it was allowed to cool, and the anhydride hydrolyzed by water. This acetic acid solution was then nearly neutralized with caustic alkali and allowed to stand for some time. White crystals of *2-methyl-3-diacetyluramino-7-nitro-4-ketodihydroquinazoline* were deposited, melting at 229–230° (corr.).

Calculated for  $C_{14}H_{13}O_6N_5$ : N, 20.17. Found: N, 20.08.

OTHER REACTIONS OF 2-METHYL-3-AMINO-5-NITRO-4-KETODIHYDRO-QUINAZOLINE.

In addition to the above, the aminoquinazoline exhibited other characteristic aniline reactions. With chloroform and potassium hydroxide solution, an isonitrile odor was obtained. With benzaldehyde, condensation occurred, apparently with formation of the benzylidene derivative, but the product was not analyzed. The aminoquinazoline was not affected by cold potassium hydroxide solution, but on warming it slowly dissolved in the alkali with a purple-red color and without liberation of ammonia. On neutralizing the alkaline solution with acetic acid, a light yellowish green fluorescent color appeared, and brownish crystals slowly separated from the solution. These were soluble in water, contained nitrogen, and melted at 259–260° (uncorr.), but were not obtained in sufficient amount to identify.

*2,2'-Dimethyl-5,5'-dinitro-4,4'-diketotetrahydrodiquinazolyl,*



—In preparing the aminoquinazoline from 6-nitroacetantranil and hydrazine hydrate, the anthranil was added to the hydrazine solution in order to keep the latter always in excess, and thus insure a monomolecular condensation. In preparing the di-



quinazolyl, on the other hand, the hydrazine hydrate was added to the anthranil, so that the anthranil might always be in excess and a dimolecular reaction secured.

The hydrazine hydrate was added to the finely powdered anthranil with constant stirring, and the solution was gently heated. The product of the reaction formed a compact yellow mass at the bottom of the beaker. This was filtered, and the residue boiled with dilute alcohol to remove any aminoquinazoline, and finally washed with dilute potassium hydroxide solution to remove any 6-nitroacetanthranilic acid which might have been formed from the excess of anthranil. The residual diquinazolyl was crystallized from a mixture of alcohol and acetone.

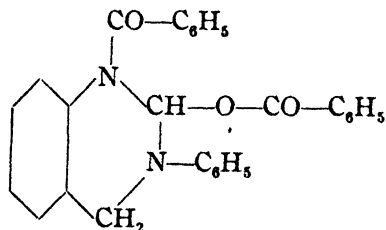
It forms small, granular crystals, which melt at  $306^{\circ}$ . It is not affected by acids or alkalis, and apparently forms no bromine derivative.

Calculated for  $C_{18}H_{12}O_6N_6$ : C, 52.74; H, 2.94; N, 20.58. Found: C, 52.32 and 52.21; H, 2.89 and 2.73; N, 20.35 and 20.15.

This same diquinazolyl was obtained by condensing the aminoquinazoline with another molecule of the acetanthranil, but the yield by this process was very poor.

*Acetic Anhydride Addition Product of the Diquinazolyl*—When the foregoing diquinazolyl was boiled with excess of acetic anhydride, it was slowly dissolved. On cooling, cubical crystals separated, which softened at  $223^{\circ}$  and melted at  $228^{\circ}$  (corr.).

This may be a substance analogous to that obtained by Heller<sup>1</sup> on treating orexine with benzoic anhydride, and to which he ascribed the following formula:



Great difficulty was experienced in analyzing both the diquinazolyl and its acetic anhydride addition product. In both cases the carbon turned graphitic. The acetic anhydride addition product exploded unless the heating was very carefully con-

<sup>1</sup> Ber. 37, 3114 (1904).

ducted, and even then no satisfactory analysis could be secured, the results, however, indicating quite clearly that only one molecule of acetic anhydride had been added to the diquinazolyl.

HAVEMEYER LABORATORIES,  
COLUMBIA UNIVERSITY,  
April, 1906.

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## A REVIEW OF RECENT PROGRESS IN PHYSICAL CHEMISTRY.

BY GILBERT N. LEWIS.

Received May 19, 1906.

It is becoming more difficult year by year to make a satisfactory survey of any given field of scientific investigation. In the last year 1644 articles were classed as physico-chemical and abstracted in the *Physikalisch-chemisches Centralblatt*. To attempt anything like a summary of this enormous mass of literature would be absurd. I shall only try in a fragmentary way to touch upon some of the larger problems of general chemistry and a few of the more noteworthy contributions toward their solution. As is customary in these reviews I shall consider only the work done in foreign lands, and I shall further restrict the field by omitting any reference to the modern developments in radioactivity and the theory of electrons, for I fear that if I should embark upon this fascinating subject little space would be left for the older problems of our science.

In no other line of physico-chemical research during the past year has there been more satisfactory progress than in the determination of the so-called free energy of chemical reactions, nor is there any work of greater importance than this to be done. Complete tables for free energy such as we now have for the heat of chemical reactions would permit the technical chemist to calculate at once the maximum amount of work which he could hope to obtain from a given reaction or the minimum amount of work necessary to effect it. It would enable the student of pure chemistry to predict under given circumstances just what reactions could occur and how nearly they would run to an end. It would be the first step towards a fuller knowledge of chemical affinity.

Since mechanical power is now the most valuable of all commodities, the great technical problem of the day is to obtain from the combustion of coal the largest possible amount of available work. Many attempts have been made to construct a galvanic cell which will consume at one electrode the oxygen of the air, at the other some kind of fuel. Several of these attempts such as the carbon monoxide cell of Borchers and the coke cell of Jacques have at first appeared successful, but in every case it has been

shown that the electromotive force obtained was the result either of thermal effects, or of some secondary reaction, and was not due to the combustion of the fuel. Haber and Moser (*Z. Elektrochem.* **11**, 593 (1905)) have now succeeded in measuring at  $445^{\circ}$  and at  $518^{\circ}$  the electromotive force of a cell in which carbon monoxide and oxygen combine reversibly to form carbon dioxide. Since the cell which they constructed is very polarizable, and gives its maximum electromotive force only when the feeblest currents are allowed to pass, it cannot be regarded as a very great step towards the perfect technical fuel cell. Still this work, together with previous data concerning the equilibria between carbon, oxygen, carbon monoxide and carbon dioxide, with which it stands in close agreement, and with the recent work of Löwenstein (*Z. physik. Chem.* **54**, 706 (1905)) on the dissociation of carbon dioxide between  $1500^{\circ}$  and  $2000^{\circ}$ , permits now a reliable calculation of the maximum work that we may hope to obtain, at any temperature, from the combustion either of coal or of carbon monoxide.

Hardly less important than the free energy of the formation of carbon dioxide is the free energy of formation of water. This is a quantity which until within a year has been regarded as known with fair accuracy. The hydrogen-oxygen cell, which was first studied by Grove in 1839, has since been the subject of numerous investigations. Its electromotive force was repeatedly found to lie between 1.08 and 1.12 volts. Very recently Westhaver (*Z. physik. Chem.* **51**, 65 (1905), using iridium electrodes instead of platinum, obtained a very well defined value of 1.06 volts. What the true significance of these values may be is a very interesting question, but it is now certain that they in no case represent the maximum electromotive force corresponding to the reversible union of oxygen and hydrogen to form water. The true value is undoubtedly a tenth of a volt higher than the highest of these. Nernst and von Wartenberg (*Göth. Nachr.* 1905, Heft 1), from the dissociation of water vapor at high temperatures, obtain 1.23 volts for the true electromotive force of the hydrogen-oxygen cell at  $25^{\circ}$ , while in this country the almost identical value, 1.22 volts, has been obtained by an entirely different method. The method of Nernst and von Wartenberg consisted in passing water vapor through a porcelain tube heated to a constant temperature between  $1000^{\circ}$  and  $2000^{\circ}$  and then through a capillary in which it was very rapidly cooled. From the quantity of hydrogen and oxygen left the dissociation of water vapor at the temperature of the hot tube was calculated. It amounted to about 0.02 per cent. at  $1500^{\circ}$  and 0.2 per cent. at  $1800^{\circ}$ . These values agree with others obtained with a different method by Löwenstein (*Z. physik. Chem.* **54**, 706 (1905)) who also worked in Nernst's laboratory. In order to calculate from the degree of dissociation at these high temperatures that at ordinary temperatures it is

necessary to know not only the heat of formation of water at ordinary temperatures but also the specific heats of the reacting substances throughout the whole temperature range. The specific heats of gases at high temperatures have hitherto been only roughly determined through a study of the maximum pressure developed in explosions. This gap is now being filled. Holborn and Henning (*Ann. Physik.* [4] **18**, 739 (1905)), at the Reichsanstalt, have recently made a thorough series of calorimetric determinations of the specific heat of water vapor between 0° and 800°.

Another equilibrium of great importance both to technical and to theoretical chemistry has been very thoroughly studied during the past year. This is the equilibrium between sulphur trioxide on the one side and sulphur dioxide and oxygen on the other. Bodenstein and Pohl (*Z. Elektrochem.* **11**, 373 (1905)), in a very complete investigation, applied successfully both the mass law and the equation (isochore) of van't Hoff to this reaction between 500° and 900°. Their results have been further corroborated by the independent work of Lucas (*Z. Elektrochem.* **11**, 457 (1905)) and these two investigations taken with the earlier work of Knietsch (*Ber.* **34**, 4093 (1901)), Bodländer and Köpper (*Z. Elektrochem.* **9**, 789 (1903)), and Lunge and Pollit (*Z. angew. Chem.* **15**, 1105 (1902)), establish within a small margin of error the data which will be fundamental in computing the free energy of all the sulphates, and which at the same time are of the highest importance for the practical development of the sulphuric acid industry.

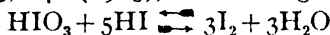
The commercial manufacture of ammonia from its elements appears now to be not only a possibility but a probability. The difficulty at present lies in the fact that at temperatures of 1000° or over, where equilibrium is quickly reached, the elements show but a slight tendency to combine and the yield of ammonia is small. On the other hand, at lower temperatures where the combination would progress much further, the reaction is exceedingly slow. The problem here is simply to find a catalyzing agent which will take the rôle that platinum takes in the oxidation of sulphur dioxide, and enable the reaction to take place rapidly at a temperature where the yield is large. Haber and van Oordt (*Z. anorg. Chem.* **43**, 111 and **44**, 341 (1905)), who have investigated fully the equilibrium between ammonia and its elements, have sought such a catalyzer in some metal which will unite rapidly with nitrogen to form the nitride but from which the nitrogen can be withdrawn by a current of hydrogen. They have so far investigated calcium and manganese but neither of these proves to be the right substance.

Much of our earlier knowledge of equilibria at high temperatures was obtained by analysis of the products of explosions. Nernst (*Z. anorg. Chem.* **45**, 126 (1905)) and Finckh (*Z. anorg. Chem.* **45**, 116 (1905)) have both shown the unreliability of this

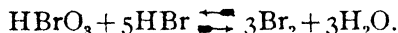
method. Its validity depends in fact upon the rather unlikely assumption that equilibrium is reached at the moment of maximum temperature and that it does not have time to change during the cooling that follows. Nernst shows, however, that by observing the maximum pressure produced by the explosion a knowledge of the equilibrium may frequently be obtained.

The whole subject of equilibria between gases at high temperatures has been most admirably presented by Haber ("Thermodynamik Technischer Gasreaktionen," R. Oldenberg, Munich and Berlin (1905)) in a treatise on "The Thermodynamics of Technical Gas-reactions." This book from an acknowledged master of both theoretical and applied chemistry contains a lucid exposition of the problems and recent developments in this important field. It is a pleasure to learn that a translation into English is soon to appear.

Of the investigations of free energy and chemical equilibrium at ordinary temperatures perhaps the most interesting is one by Luther and Sammet (*Z. Elektrochem.* **11**, 293 (1905)); (Sammet: *Z. physik. Chem.* **53**, 641 (1905)) concerning the reactions,



and



Both of these reactions run so nearly to an end that all the reacting substances cannot exist together at concentrations which can be determined by analytical methods, but it was found possible in the first case to determine the equilibrium by using as the source of iodide ion the difficultly soluble silver iodide whose solubility product is known. The iodide ion concentration

was then so small that the remaining substances ( $\text{IO}_3^-$ ,  $\text{H}^+$ ,  $\text{I}_2$ ) taking part in the reaction existed in equilibrium in quantities sufficient for analytic determination. Equilibrium was reached at 25° in seven weeks, at 60° in four days. At each temperature the mass law was followed, according to the equation,

$$\frac{\text{H}^+(\text{IO}_3^-)(\text{I})^5}{(\text{I}_2)^3} = K,$$

and the values of K found for the two temperatures were consistent with the equation of van't Hoff. The same reaction was studied in an independent way by the determination of the electromotive force of the cell  $\text{Pt}(\text{IO}_3^-; \text{H}^+; \text{I}_2) - (\text{I}_2; \text{I}^-)\text{Pt}$ . This was found by direct measurement to be 0.549 volt, while from the value of K the authors calculated likewise 0.549 volt, a remarkably good agreement. Furthermore, the electromotive force of this cell varied with varying concentrations of the different substances in good agreement with theory. Theory demands that the oxidation potential of any oxygen acid such as per-

manganic, chromic, etc., should depend upon the concentration of the hydrogen ion, but this is the first case in which it has been found possible to verify this theory and obtain a truly reversible potential. It is indeed the first time that any single reversible potential has been measured, which depends upon the concentration of three substances ( $\bar{\text{IO}}_3, \text{H}^+, \text{I}_2$ ).

In the midst of this rapid progress toward a fuller knowledge of chemical affinity it is with something of a shock that we read (DeForcrand, *Compt. rend.* **139**, 906 (1904)) that Berthelot's principle of maximum work is the only sure guide to chemical affinity. In another article (*Compt. rend.* **139**, 908 (1904)) the same author (DeForcrand) admits that there are slight corrections to be applied in using this principle, but maintains that only from the heat of reaction can we predict whether or not a reaction will occur. There is something pathetic in this loyal allegiance to a lost cause. Experiments are now being extended to temperatures at which the principle of Berthelot can only be true in rare cases. Indeed at the temperature of the electric furnace it will probably be found a pretty general rule that *only those reactions occur which are accompanied by an absorption of heat.*

But while denying the factitious importance given to thermochemical data by the principle of Berthelot there is danger that we may underestimate their real value. In the future these data will be required especially in calculating the conditions of chemical equilibrium at one temperature from those at another, and there is even now an immediate need for an accurate revision of thermochemical measurements, for even such important data as the heat of formation of water and hydrochloric acid are known with little accuracy. That it is possible with methods now available to make much more accurate thermochemical measurements than the majority of those that are to be found in the literature is shown by an investigation of Wörmann (*Ann. Physik.* [4] **18**, 775 (1905), and *Inaug. Dissert. Münster i. W.* (1905)) upon the heat of neutralization of strong acids and bases and its change with the temperature, the latter being found to be almost exactly linear. The results obtained have furthermore an intrinsic value in that they permit the calculation of the degree of electrolytic dissociation of water at all temperatures from the degree of dissociation at any one temperature.

At the same time new improvements are constantly being made in calorimetric methods and new investigations on the fundamental units of energy. Dieterici (*Ann. Physik.* [4] **16**, 593 (1905)) and Behn (*Ann. Physik.* [4] **16**, 653 (1905)) have studied the ice calorimeter and have obtained independently almost identical values for its characteristic constant. They both determined also the ratio between the mean calorie and the

15° calorie and their results agree closely with each other and with the work of Barnes. Dieterici investigated the specific heat of liquid water throughout the whole range from 0° to 300°, and incidentally found a value for the mechanical equivalent of heat which agrees well with the best previous results and for which the author claims an accuracy within 0.05 per cent.

Dewar (*Proc. Roy. Soc.* 76 A, 325 (1905)) has continued his researches upon the liquid air and the liquid hydrogen calorimeters and shows that with the former it is possible to detect 0.02, with the latter 0.003 of a gram-calorie. With these calorimeters he has determined the specific heats of several substances at low temperatures. The value for diamond between -188° and -252.5°—namely, 0.0043—is the smallest that has been obtained for any solid substance. Dewar (*Proc. Roy. Soc.* 74 A, 122 (1904)) has also continued his investigations on the absorption of gases by charcoal at low temperatures, and finds that this absorption increases rapidly with decreasing temperature. The author might have predicted this thermodynamically for he has found that the absorption is always accompanied by a considerable evolution of heat; indeed, this heat in the case of hydrogen, nitrogen and oxygen is greater than the heat of liquefaction. This phenomenon is doubtless closely connected with the evolution of heat which has been observed at ordinary temperature when fine powders, such as silica or charcoal, are moistened with liquids.

Other interesting work at low temperatures has been done by Valentiner (*Ann. Physik.* [4] 15, 74 (1904)), who has determined the ratio  $C_p/C_v$  for nitrogen, at the temperature of liquid air, where it behaves like a pretty imperfect gas, and by Olszewski (*Ann. Physik.* [4] 17, 986 and 994 (1905)) who attempted to liquefy helium by allowing it to cool by sudden expansion from 180 atmospheres at -259°. In this process the author estimates that the gas was cooled to within 1.7° of the absolute zero but no sign of liquefaction appeared.

Turning to the subject of reaction velocity, we find a large and rapidly accumulating mass of literature, much of which is of a character too detailed for discussion in a review of this kind; nor are there lacking articles in this field which contain speculations of such fantastic character that they threaten to retard rather than promote real progress.

An interesting point in the general theory of reaction velocity is raised by Brunner (*Z. physik. Chem.* 51, 106 (1905)), who shows the untenability of the commonly accepted notion that the velocity is proportional to the quotient of the driving tendency of the reaction, as measured by its free energy, divided by a certain more or less constant chemical resistance. Brunner points out that at the beginning of a reaction, before any of the products are formed, the momentary tendency to react is infinite while the velocity is undoubtedly always finite.

The theory of Nernst (*Z. physik. Chem.* **47**, 52 (1904)) and Brunner (*Z. physik. Chem.* **47**, 56 (1904)), that the speed of every heterogeneous reaction is simply the speed of diffusion of the reacting substances toward the surface separating the two phases, has not been substantiated. Thus Goldschmidt (*Z. Elektrochem.* **11**, 430 (1905)), studying the speed of ester saponification in heterogeneous systems, finds several cases in which the reaction velocity in the homogeneous phase is the determining factor, and Brunner (*Z. physik. Chem.* **51**, 494 (1905)) himself finds in the solution of arsenic trioxide an example of a reaction whose velocity is determined by the speed of a chemical process in the surface film itself. Brunner here adheres to the theory in a modified form, but the modification consists practically in the denial of the original theory. The views of Nernst and Brunner have, however, helped to bring about a recognition of the real importance of processes of diffusion in heterogeneous reactions.

It is now generally admitted that most of the gaseous reactions which have been studied do not take place in the homogeneous gaseous phase, but upon the surface of the containing vessel. One of the most interesting cases of this kind has been studied by Bodenstein and Ohlmer (*Z. physik. Chem.* **53**, 166 (1905)) who, after showing that the union of carbon monoxide and oxygen occurred chiefly on the surface of the glass vessel in which they were contained, attempted to diminish this action of the walls by using tubes of fused quartz. Instead they found a much greater catalytic effect than before. In studying further this phenomenon the authors came to the very remarkable conclusion that the catalytic action of the silica is reduced by the presence of carbon monoxide and to a greater extent the greater the concentration of carbon monoxide. We have here therefore the curious case of a substance acting as a negative catalyzer to a reaction in which it itself takes part. This new phenomenon the authors term negative autocatalysis. It seems to me that their work may furnish a clue to one of the most mysterious of chemical phenomena. It was Davy who first noticed that phosphorus glows in air but not in pure oxygen, and in general that it glows more brightly the smaller the concentration of oxygen in contact with it. Since then the same phenomenon has been observed in the combustion of hydrogen phosphide, and in fact of most other gases. If now it can be shown that all these reactions take place only at the surface of some solid, and that the catalyzing action of the surface is reduced by the presence of oxygen, the phenomenon would be completely analogous to that observed by Bodenstein and Ohlmer.

An interesting case of catalysis has been observed by Bredig and Fraenkel (*Z. Elektrochem.* **11**, 525 (1905)) in the decomposition of ethyl diazoacetate. The rate of this decomposition is enormously affected by the presence of even very dilute acid.



The reaction therefore promises to be serviceable as an indicator by which small concentrations of hydrogen ions may be quantitatively determined as, for example, in estimating the degree of hydrolysis of slightly hydrolyzed salts.

Much attention has been given recently to the application of physico-chemical methods to the study of the dynamic isomers and their rates of transformation. Of especial interest to organic chemists is the work on the desmotropic compounds, carried on by Dimroth (*Ann.* **335**, 1 (1904) and **338**, 143 (1905); *Z. Elektrochem.* **11**, 30 (1905)), Brühl and Schroeder (*Z. physik. Chem.* **50**, 1 (1904); *Ber.* **37**, 3943 (1904)), Goldschmidt (*Z. Elektrochem.* **11**, 5 (1905)) and others.

It has been pointed out by LeBlanc (*Z. Elektrochem.* **11**, 9 (1905)) that the problem of the passive state of metals is essentially a problem in reaction velocity and that a metal is passive when the reaction by which the metal enters solution in the ionic condition is in some way greatly retarded. But what the nature of the resistance is which causes this retardation and why it suddenly appears and as suddenly disappears is still an unsolved problem. Much interest has lately been shown in this puzzling phenomenon. Müller (*Z. Elektrochem.* **11**, 755 (1905)) has studied passive zinc and manganese, Ruer (*Z. Elektrochem.* **11**, 661 (1905)), passive platinum; Babrovski (*Z. Elektrochem.* **11**, 465 (1905)) has published a very interesting article on passive magnesium, and Sackur (*Z. physik. Chem.* **54**, 641 (1905)) has even gone so far as to speak of passive hydrogen. It is doubtful whether in all these cases the phenomenon is really of the same character as that which is observed in the case of iron and chromium.

The use of a reversible iron electrode in the new Edison-Jungner storage cell seems at first sight inconsistent with the marked tendency of iron to assume the passive state, especially in alkaline solutions. This point led to an interesting discussion in the *Bunsen Gesellschaft* by Elbs (*Z. Elektrochem.* **11**, 734 (1905)), Foerster (*Z. Elektrochem.* **11**, 948 (1905)), Gräfenberg (*Z. Elektrochem.* **11**, 736 (1905)) and Müller (*Z. Elektrochem.* **11**, 949 (1905)). It was shown in fact that when the cell is filled, special precautions must be taken to make the iron active, and that the degeneration of the cell, which has sometimes been observed, is probably due to the gradual assumption of the passive state. This may be retarded by various devices, for example, a trace of mercury apparently acts catalytically to prevent passivity.

No entirely satisfactory theory of passivity has yet been advanced. The old oxide film theory still has its supporters although it has now been definitely shown that such a film must be a good electric conductor and must be so thin that the optical properties of the metallic surface remain unchanged. In connection with this theory it would be interesting to see if the

phenomenon of passivity could be obtained in some solvent such as liquid ammonia, which contains no oxygen. Perhaps the most plausible among the various explanations of passivity is that offered by Kruger and Finkelstein (*Z. physik. Chem.* **39**, 91 (1902)). According to their idea a metal like iron contains both ferric and ferrous iron, is an alloy, as it were, of the two. In equilibrium there is a certain ratio between the quantities of the two, but when the equilibrium is once disturbed it is restored only with extreme slowness. When iron is acted on by an oxidizing agent only the ferrous portion dissolves, leaving a film of ferric iron, which behaves as a noble metal until more ferrous iron is produced from it, or until it is mechanically broken so that a new portion of metal is exposed. Müller (*Z. Elektrochem.* **11**, 823 (1905)) has recently proposed a new theory, based on the idea of electrons, which appears to be essentially a development of this theory of Kruger and Finkelstein.

Ruer (*Z. Elektrochem.* **11**, 661 (1905)) assumes passivity in platinum in order to explain the fact that platinum electrodes do not go into solution when made the anodes with a direct current, but are readily attacked by an alternating current. Presumably the platinum anode is soon rendered passive by the direct current and therefore ceases to dissolve, while with the alternating current each cathodic polarization restores the activity of the metal. This view is borne out by the fact that certain oxidizing agents have practically no action on platinum, but the platinum goes into solution when dipped alternately into the oxidizing agent and some reducing agent.

A good deal of work has been done recently upon electrolysis by the alternating current. Brochet and Petit (*Ann. chim. phys.* [8] **3**, 433 (1904); *Compt. rend.* **139**, 855 (1904); *Z. Elektrochem.* **10**, 909 and 922 (1904) and **11**, 441 (1905)) have studied especially those reactions which may have a technical significance. LeBlanc (*Z. Elektrochem.* **11**, 8 and 704 (1905)), by determining under what conditions a metal is dissolved during the passage of an alternating current, hopes to find evidence concerning the speed of formation of a complex ion from its constituents, for he argues that under ordinary circumstances a metal will dissolve during one phase of the alternating current, but redeposit in the same quantity during the reverse phase. If, however, the metallic ions formed during the first phase are removed—or example by the formation of a complex—before the phase changes, then the metal will fail to deposit and the total result will be the gradual solution of the metal. LeBlanc explains in this way the solution of copper by an alternating current in a solution of a substance like a cyanide which forms complexes with the copper ion. He hopes to be able to calculate the speed of formation of such a complex from the influence of the frequency of alternation of the current upon the amount of copper dissolved. It is doubtful,

however, whether he has given sufficient consideration to other factors which enter into the problem.

This question of the speed of formation of a complex ion from its components, and *vice versa*, has been given prominence by an article of Haber (*Z. Elektrochem.* 10, 433 and 773 (1904)). Electromotive force measurements show that the concentration of silver ion in a normal solution of potassium silver cyanide is about  $10^{-23}$  normal, or perhaps half a dozen single ions in a liter. It has been supposed that such figures have a purely statistical significance, and mean not that half a dozen particular silver atoms exist continuously in the condition of simple ions while all the rest of the silver ions remain in the complex ions, but rather that all the silver atoms alternate, with unknown frequency,

between the two conditions expressed by the symbols  $\overset{+}{\text{Ag}}$  and  $\text{Ag}(\text{CN})_3$ , and that any one atom on the average remains in the

$\overset{+}{\text{Ag}}$  condition  $10^{-23}$  part of the time. Now Haber doubts whether these small concentrations calculated by the Nernst equation have even so much meaning. His ingenious argument is somewhat as follows: When equilibrium is established in the system,

$\overset{+}{\text{Ag}} + 3\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_3$ , the reaction velocities in both directions must be equal, although the substances on the left-hand side are present in extraordinarily small concentrations. Assuming that the velocity of their combination would increase with their concentration, according to the principle of Guldberg and Waage, Haber calculates that if a solution could be prepared normal both in silver and in cyanide ions they would unite  $10^{23}$  times as

fast as a normal solution of  $\text{Ag}(\text{CN})_3$  dissociates. Now the latter reaction has been generally assumed to be fairly rapid, since silver can be readily precipitated from the cyanide, either by a sulphide or by the electric current. Choosing for this rate what he considers a reasonable value, Haber obtains for the velocity of combination in the hypothetical normal solution of  $\overset{+}{\text{Ag}}$  and  $\text{CN}^-$  a

velocity so great that to interpret the reaction in the usual way we should be obliged to conceive of the atoms moving together with a velocity millions of times greater than the velocity of light. We thus reach an absurd conclusion which apparently is based solely upon (1) the Nernst equation (2) the principle of Guldberg and Waage, and (3) the general atomistic conception. A lively discussion following the publication of this paradox was participated in by Danneel (*Z. Elektrochem.* 10, 609 (1904)), Abegg (*Z. Elektrochem.* 10, 607 (1904)) and Bodländer (*Z. Elektrochem.* 10, 604 (1904)). The latter pointed out what appears to be the real solution of the problem. Haber's whole argument rests on the assumption that the complex silver cyanide ion dissociates

with fair rapidity into its constituents, and this is in turn based solely on the fact that silver is readily precipitated from the cyanide solution. Obviously, the tacit assumption is here made that the complex ion can enter into no reaction without first splitting into its ions. If this entirely gratuitous assumption is omitted, the whole paradox disappears. The assumption that reactions in aqueous solution take place only between ions is itself one which I presume the majority of physical chemists have never adopted and which certainly has now been shown by the experiments of Kahlenberg and others to be directly opposed to all the evidence. Walker (*Trans. Chem. Soc.* **85**, 1082 (1904)) has also recently contributed a number of arguments in opposition to this view.

Much work remains to be done before we can form any adequate conception of the conditions that actually exist in an aqueous solution of an electrolyte. Walker (*Z. physik. Chem.* **51**, 706 (1905)) has shown that a considerable number of weak electrolytes which were formerly supposed to form exceptions to the mass law belong to the class of amphoteric electrolytes, that is, substances which are capable of yielding simultaneously hydrogen and hydroxyl ions. When this complication is taken into consideration all these substances are found to behave normally. On the other hand, no complete explanation has yet been offered for the deviation of strong electrolytes from the Ostwald dilution law, and it is still an open question whether this deviation is apparent or real. Jahn (*Z. physik. Chem.* **50**, 129 (1904)) adheres to his idea that the deviation is in the main apparent and caused by an increase in the velocity of the ions in strong solution, whereby their concentration as measured by the conductivity method appears greater than it really is. In support of this view he has recently made a number of freezing-point determinations of solutions of strong electrolytes and calculates from these the concentrations of the ions and of the undissociated salt. He shows that the values thus obtained agree with the (somewhat modified) dilution law. But there is some doubt as to whether freezing-point determinations are yet sufficiently accurate for this kind of calculation. Goebel (*Z. physik. Chem.* **53**, 213 (1905)), for example, points out that the freezing-point law of van't Hoff is not quite true and that a correction should be made for the change in the heat of fusion of ice with the temperature. Applying this correction to existing data upon various salts he shows that they then become consistent with the mass law. Drucker (*Z. Elektrochem.* **11**, 904 (1905)), however, shows that Goebel made use of unreliable data for calculating the heat of fusion of ice. A matter of fact the true correction is only about one-half of that used by Goebel, but is nevertheless large enough to be taken into consideration in exact work.

The method of Rothmund and Drucker for determining the degree of dissociation of strong acids, by studying their distribution between water and a non-miscible organic solvent, has been further employed by Drucker (*Z. physik. Chem.* **49**, 563 (1904)) and by Bogdan, (*Z. Elektrochem.* **11**, 824 (1905)) with rather uncertain results.

A most interesting point, especially in its connection with the views of Jahn, has been raised by Danneel (*Z. Elektrochem.* **11**, 249 (1905)). It has often been noted as an interesting fact, that the two ions which move most rapidly in aqueous solution, hydrogen and hydroxyl, are the component ions of the water itself. Now it has been shown independently by Tijmstra (*Z. physik. Chem.* **49**, 345 (1904)) and by Dempwolff (*Physik. Z.* **5**, 637 (1904))

that in methyl alcohol the ion  $\text{CH}_3\text{O}$  travels with exceptional speed, and Danneel concludes that in general the ions of the solvent move faster than others and that this is due to their ability, so to speak, to go through a solvent molecule rather than around it. In other words, the neutral molecules play a rôle in the conduction similar to the one that was ascribed to them by the old Grotthuss theory. If this view is correct, the ions of a salt should likewise move more rapidly in the presence of the neutral salt, that is, in concentrated solutions, as Jahn believes that they do. Why this same effect is not shown to an even greater extent in the case of the weak electrolytes, in which the proportion of the undissociated substance is much greater, Danneel does not attempt to explain. Whatever the probability may be of a material change in the ionic velocities at high concentrations, the best evidence seems to show that at least below concentrations of tenth-normal the electrical conductivity furnishes a good, at any rate the best, measure of the degree of dissociation, and that here there is a real deviation from the mass law. The idea seems to be gaining ground that this deviation is due to change in the dissociating power of the solvent caused by the addition of the electrolyte. All the recent views concerning the "Anomalies of Strong Electrolytes" have been brought together in an excellent monograph by Drucker "Die Anomalien der Starken Elektrolyte," Ahren's Sammlung X, 1 and 2, Enke, Stuttgart, (1905).

Continued investigation of conductivity in non-aqueous solutions, instead of bringing an answer to the problem of the real nature of electrolytic conductivity, serves rather to show how far we still are from the final solution of this question. Who would have thought a few years ago of classing ether as an electrolyte or as an electrolytic solvent? Yet Plotnikow (*J. Russ. physik. chem. Soc.* **36**, 1282 (1904)) has shown that a solution of phosphoric acid in ether conducts one-third as well as its solution in water, while Steeple, McIntosh and Archibald (*Phil. Trans.* **205**

A, 99 (1905)) have found that ether dissolved in liquid hydrochloric acid is an excellent electrolyte.

One of the most extensive researches in this subject is by Walden (*Z. physik. Chem.* 54, 129 (1906)) on organic solvents. His method of attack is unique, in that he chooses some particular solute, especially tetraethylammonium iodide, which he takes as "normal electrolyte" and studies its solution in a large number of solvents. In this way he has been led to several interesting generalizations, two of which may be mentioned here. The first concerns the relation between dielectric constant and dissociating power and may be stated as follows. If two solutions of the same electrolyte in different solvents are taken at such dilutions

that the degree of dissociation is the same in both then  $\frac{E_1}{E_2} = \frac{v_2}{v_1}$  or  $E\nu = \text{const.}$ , where  $E_1$  and  $E_2$  represent the two dielectric constants,  $v_1$  and  $v_2$  the dilutions. This is only an approximate law but it is the first successful attempt to obtain any sort of quantitative relation between dielectric constant and dissociating power. The second purely empirical principle relates to the conductivity at infinite dilution. The smaller the value of this quantity is in a given solvent, the greater is its temperature coefficient. In other words, the values of the conductivity at infinite dilution in different solvents approach each other with increasing temperature.

Another paper deserving special mention is one by Steele, McIntosh and Archibald (*Phil. Trans.* 205 A, 99 (1905)) on hydrogen chloride, bromide, iodide, and sulphide as conducting solvents. The authors have made a very thorough study of the properties of these liquids, especially the first three, and they have determined the vapor-pressures, surface tensions, and densities of the pure solvents and the molecular weights, the transport numbers and the conductivity of their solutions. They obtain a remarkable result in determining the molecular weight of toluene in hydrochloric acid. The value found is 30, or about one-third of the normal molecular weight. Yet the solution is a non-conductor.

Hydrogen sulphide as a solvent has also been studied by Antony and Magri (*Gazz. chim. ital.* 35, 208 (1905)). Schroeder (*Z. anorg. Chem.* 44, 1 (1904)) has studied solutions in pyridine, and Walker and Johnson (*Trans. Chem. Soc.* 87, 1597 (1905)) solutions in acetamide. Most of these observers have found numerous cases in which the molecular conductivity in dilute solutions increases with the concentration. Indeed, this behavior seems to be characteristic of a very large class of non-aqueous solutions. It is not improbable that this is an extreme manifestation of the same phenomenon that is responsible for the deviation from the mass law in aqueous solutions. In both cases the molecular

conductivity at low concentrations is smaller than was to be predicted.

In many of the investigations that we have mentioned it has been shown that the solutes which give conducting solutions are able to form definite solid compounds with the solvent, thus indicating that probably in the solution, too, there is a union of solvent and solute. For example ether and toluene dissolved in hydrochloric acid differ in that the former is a conductor, the latter is not. Ether forms definite compounds with the solvent, while toluene does not. It now seems probable indeed that the formation of an electrolytic solution is usually, if not always, accompanied by "solvation." The belief is sometimes expressed that this solvation is the immediate cause of electrolytic dissociation. This view is discussed by Bousfield (*Z. physik. Chem.* **53**, 257 (1905)) who elaborates the idea of Kohlrausch (*Proc. Roy. Soc.* **71**, 338 (1903)) that each ion in aqueous solution is surrounded by an "atmosphere" of water molecules.

Domke and Bein (*Z. anorg. Chem.* **43**, 125 (1905)) have reopened a question which a few years ago was answered, rather too dogmatically, in the negative, namely, whether from the density and other physical properties of aqueous sulphuric acid it is possible to obtain evidence of the existence of definite hydrates in solution. They carried out, apparently with the highest accuracy, an exhaustive series of experiments upon the density and coefficient of expansion of sulphuric acid of different strengths. Although cautious about drawing conclusions from their data, they believe that their work taken in conjunction with the measurements of other physical properties by other experimentors furnishes strong grounds for the belief that a mixture containing sulphuric acid and water in equimolecular proportions consists almost entirely of the substance  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . As to the existence of other hydrates the evidence is less conclusive.

In the study of colloids little progress has been made since the very complete review of this subject by Professor Noyes, which recently appeared in this Journal (**27**, 85 (1905)). Billitzer's (*Z. physik. Chem.* **51**, 129 (1905)) theory of colloids will probably not find very wide acceptance until his experimental results have been better corroborated than they have been hitherto. Sutherland (*Phil. Mag.* [6] **9**, 781 (1905)) has worked out a theory of diffusion for non-electrolytes and applies it to a solution of egg albumen. From the rate of diffusion of this substance he obtains for it a molecular weight of 32,814 and gives it the formula  $\text{C}_{1438}\text{H}_{2164}\text{N}_{35}\text{O}_{43}\text{S}_{15}$ . The calculation rests, however, upon a pretty hypothetical basis.

Benedicks (*Z. physik. Chem.* **52**, 733 (1905)) believes that in one of the constituents of steel he has found a case of solid colloidal solution. Brown (*Ann. Physik.* [4] **16**, 166 (1905)) tries to show that the solutions of metals in liquid ammonia are colloidal in

character. He would probably have considerable difficulty in reconciling his theory with the great lowering of the vapor-pressures which has been observed in these solutions by Franklin and Kraus, Joannis, and others.

The apparent success of the calculations of Arrhenius and Madsen upon the toxins, antitoxins, etc., have led some chemists to regard these substances as true solutions. Henri (*Z. physik. Chem.* **51**, 19 (1905)) has brought them back to what is undoubtedly their true place, under colloidal suspensions, in an important article entitled "Enzymes, Toxins, Antitoxins and Agglutinins."

While renewed interest in atomic weights has been aroused by several new and very accurate analyses, more recognition has also been given during the past year to the new physico-chemical methods of determining atomic weights. These methods all depend upon the assumption that every gas, as its pressure is diminished, approaches a perfect gas. In other words, the law of Avogadro, that under like conditions the molecular weights of gases are proportional to their densities, is a true limiting law for all gases as their pressure is indefinitely diminished. Therefore, if the density of any gas compared with oxygen is known, and the coefficient of compression of both gases between 0 and 1 atmosphere, the molecular weight of the gas can be exactly determined.

This method has been applied by Berthelot (*Z. Elektrochem.* **10**, 621 (1904)), Guye (*Compt. rend.* **140**, 1386 and 1241 (1905)), Leduc (*Compt. rend.* **140**, 717 (1905)), Rayleigh (*Proc. Roy. Soc.* **74**, 446 (1905); *Z. physik. Chem.* **52**, 705 (1905)), Jaquero and Scheuer (*Compt. rend.* **140**, 1384 (1905)) and others. Guye, for example, obtained the following values  $S = 32.065$ ,  $C = 12.002$ ,  $Cl = 35.476$ ,  $Ar = 39.866$ , all of which agree excellently with the atomic weights obtained by analytic methods. For nitrogen, on the other hand, the results obtained by this method are all lower than that found by Stas, 14.04. Thus the different investigators obtained the following results: Berthelot, 14.007; Leduc, 14.008; Rayleigh, 14.007; Guye, from the comparison of the four pairs of gases— $N_2, O_2$ ;  $N_2, CO$ ;  $N_2O, CO_2$ ;  $NO, O_2$ —finds 14.009, 14.006, 14.007, 14.008. Jaquero and Perrot (*Compt. rend.* **140**, 1542 (1905)) determined the coefficients of expansion of several gases between  $0^\circ$  and  $1067^\circ$ , the melting-point of gold, and thus found the densities at the higher temperature. At this temperature Avogadro's law appears to hold even at atmospheric pressure. The atomic weight of nitrogen calculated from its density at this temperature is 14.008. From the remarkable agreement of all these values we may conclude that the true atomic weight of nitrogen is not far from 14.008. Guye (*Bull. oc. chim.* **33**, 1 (1905)) has in fact recently obtained the value 14.009 by an analytical method. Gray (*J. Chem. Soc.* **87**, 1601-1620) has also found the value 14.010 by an analytical method.

This work has also been of great importance in another way.



From the calculations used in getting the above results it is possible to determine the fundamental constants of a perfect gas. According to Berthelot the volume of 1 gram-molecule of a perfect gas at  $0^{\circ}$  and 760 mm. (latitude of  $45^{\circ}$ ) is 22.412 liters, and the absolute zero of temperature on the perfect gas scale is  $-273.09^{\circ}$  C.

The chief contributions made recently toward the solution of the problem of chemical valence have been by two men, Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig, F. Vieweg and Son (1905)) and Abegg (*Z. anorg. Chem.* 39, 330 (1904)). The appearance of Werner's book enables us for the first time to survey the whole of this author's extensive work, collected in a compact and systematic form. Werner has worked so independently and there have been so few points of contact between his work and the general development of theoretical chemistry, that it is difficult to find the right perspective for judging his views of chemical composition. No one can doubt the immense value of the great mass of experimental material which he has accumulated and it seems likely too that many of his theories, especially the idea of the coördination number, will in some form or other find a permanent place in chemistry; on the other hand, the treatment is unquestionably one-sided, and suffers from some apparent confusion between the concepts of affinity and valence and from a failure to give full recognition to the polar character of valence.

This idea of polarized valence, which is essentially the electrochemical theory, has been clearly stated by Abegg. Distinction must be made between positive and negative valence. Thus the valence of sulphur in sulphur trioxide is +6, that in hydrogen sulphide is -2. The difference between the two valences is 8 and not 4 as frequently stated. Thus it requires 8 units of an oxidizing substance, or 8 equivalents of an electric current to convert a sulphide into a sulphate. Likewise, the valence of nitrogen is -3 in ammonia, +5 in nitric acid; that of iodine is -1 in the iodides, +7 in the periodates. As in these cases so in general the difference between the extreme positive and the extreme negative valence which an element (especially a non-metallic element) can exhibit is usually eight and never more than eight. For the marked prominence of this number eight in the valence theory no explanation has been offered. Doubtless the natural arrangement of the elements in eight groups is a cognate fact.

An interesting question has been raised by LeBlanc (*Z. Elektrochem.* 11, 813 (1905)), Can one element form both positive and negative ions? It appears from the experiments of LeBlanc as well as from those of Müller and Lucas (*Z. Elektrochem.* 11, 521 (1905)), and Müller and Nowakowski (*Z. Elektrochem.* 11, 931

(1905)), that tellurium, which lies on the border line between metals and non-metals, can go into electrolytic solution like any metal at the anode, and can also go into solution as  $\overline{\text{Te}}$  at the cathode.

The correctness of Lehmann's views on the nature of liquid crystals may now be regarded as pretty definitely established. Tammann (*Z. Elektrochem.* **11**, 955 (1905)) still holds to the view that the so-called crystalline liquid is a suspension, not a homogeneous substance, but he not only has offered no explanation of why an emulsion should form when the solid crystals melt, but all attempts to separate the supposed emulsion into its components have been in vain. De Kock (*Z. physik. Chem.* **48**, 128 (1904)) repeats Tammann's own experiments and obtains results incompatible with the emulsion theory. Bredig and Schukowsky (*Ber.* **37**, 3419 (1904)) have subjected the liquids to cataphoresis without effecting any separation. Rotarski and Zemcuznyj (*Ann. Physik.* [4] **17**, 185 (1905)) have followed the cooling curve of azoxyanisol and azoxyphenetol from a higher temperature through the temperature at which the transition from the anisotropic to the crystalline liquid appears. A definite transition accompanied by a considerable heat change should produce a marked discontinuity in the cooling curve at the temperature of transition. As a matter of fact the curves of cooling showed only an extremely slight irregularity at the transition point. The authors believe that this is a strong argument against Lehmann's and for Tammann's theory, but it need not be so regarded, for Schenck (*Z. Elektrochem.* **11**, 951 (1905)) had already pointed out that the heat of transition from crystalline liquids to ordinary liquids must be very small, as evidenced by the very large change in transition point caused by impurities. A good summary of the arguments in favor of the Lehmann theory as well as of the recent developments in the study of mixed liquid crystals and other branches of the subject, is contained in a new book by Schenck ("Kristallinische Flüssigkeiten und flüssige Kristalle," W. Engelmann, Leipzig, (1905)).

The problems of photochemistry may be divided into those concerning the action of light upon chemical reactions and those which concern the absorption and emission of light by chemical substances. By far the most important recent investigation in the former field is one by Luther and Weigert (*Z. physik. Chem.* **51**, 297 (1905)). Luther studied for the first time a few years ago a case in which light affects not merely the speed of reaction but also the equilibrium of a chemical process. This was the decomposition of silver chloride to silver subchloride and chlorine. There has been some doubt, on account of the difficulty in determining the real nature of the solid phases concerned, as to whether this was a true reversible photochemical reaction. Now Luther

and Weigert have found a homogeneous reaction, that between anthracene and dianthracene, which takes place in opposite directions in the light and in the dark. The formation of anthracene from dianthracene runs in the dark practically to an end, but in the light a certain amount of dianthracene is formed from the anthracene, and this is true whether the substance is in the solid, gaseous, or dissolved state. The system in the light is in a sort of dynamic equilibrium in which the percentage of dianthracene depends directly upon the amount of light which enters.

It is possible that in certain galvanic cells whose electromotive force changes in the light we have another instance of real displacement of equilibrium. A number of such cells has been studied by Wilderman (*Proc. Roy. Soc.* **74**, 369 (1905)).

In the domain of photography Sheppard and Mees (*Proc. Roy. Soc.* **74**, 447 (1905) and **76**, 217 (1905)) have elaborated a theory of the dynamics of photographic development which, if correct, possesses both theoretical and practical importance. A monograph by Luther ("Die Aufgaben der Photochemie," Antrittsvorlesung gehalten an der Univ. zu Leipzig, July (1905)) clearly outlines the present state of photography and its problems.

An exhaustive study of the emission of light by chemical substances and reactions, especially the phenomena known as chemiluminescence, triboluminescence and crystalloluminescence has been made by Trautz (*Z. physik. Chem.* **53**, 1 (1905)). Guichant (*Rév. gén. sciences* **16**, 683 (1905)) has also published a review of the work that has been done in this comparatively unknown domain.

Fundamental work upon the phenomenon of phosphorescence has been done by Lenard and Klatt (*Ann. Physik.* [4] **15**, 225 and 425 and 633 (1904)), and by Waentig (*Z. physik. Chem.* **51**, 435 (1905)). The former investigators attempted to determine just what conditions are essential to phosphorescence in the case of the sulphides of the alkaline earths. They established the fact that the sulphide does not phosphoresce when pure and that, moreover, two impurities must be present, one a compound of a heavy metal, the other a compound of an alkali metal. Waentig believes that the phosphorescence is due to a slow reaction by which the system passes from an unstable to a stable condition. An argument in favor of this theory is that the power of phosphorescence disappears permanently when the substance is heated or subjected to heavy pressure.

## NEW BOOKS.

**CHEMISTRY OF THE PROTEIDS.** By GUSTAV MANN, M.D., B.Sc. (Oxon.),  
University Demonstrator of Physiology, Oxford. London and New  
York: Macmillan & Co. 1906. Price, \$3.25.

This book is the most serious attempt yet made to give an account of our present knowledge of the proteins. It was the author's first intention to make a translation of the second edition of Cohnheim's "*Chemie der Eiweisskoerper*," but as so much new matter was added he decided to assume full responsibility for the work and acknowledge his indebtedness to Cohnheim.

Most of the new matter consists in theoretical explanations of the physical properties of the proteins, colloids being treated at great length, and the pseudoacid pseudobasic nature of the proteins is considered to be a matter of such importance that it is extensively discussed. The author places much confidence in many recent investigations by physical chemists which have been made with egg-white or with crude mixtures of protein with other and unknown substances. Such experiments manifestly cannot be used as a basis for generalizations until they have been confirmed by repetition with pure material of definite character, and extended to many of the widely differing forms of proteins. Mann, however, appears to accept such data as satisfactory, and explains the processes by which the supposed phenomena result, although it seems to the reviewer to be too early to attempt such generalizations and explanations.

The statement of the physical properties of the proteins both in this book and in that of Cohnheim will require very serious revision as soon as the vegetable proteins are taken into consideration.

It is remarkable that so little attention has been paid to the proteins of seeds, for these offer one of the best opportunities that we have for isolating and studying these substances under comparatively definite and simple conditions. Although Mann says of vegetable proteins, "The seeds, on the other hand, with their large amount of stored albumin, have been investigated very thoroughly. Starting with Liebig, a large number of papers have been published dealing with these readily accessible and economically very important bodies," nevertheless he devotes to this part of his subject only six pages out of the six hundred and more which the book contains. Furthermore, these six pages are

crowded with incorrect statements, which an examination of the literature would have made impossible. The treatment of this part of his subject is in the highest degree unsatisfactory, and had much better have been omitted entirely.

Many of the terms employed by Mann are unusual. Thus, although the title of the book is "Chemistry of the Proteids," these bodies in the text are collectively called albumins, a practice which brings the author into confusion when he undertakes to distinguish between globulins and the group of water-soluble proteins commonly known as albumins.

Coagulation is made synonymous with precipitation, and acid albumin and coagulated albumin appear to be regarded by the author as one and the same thing, although the product of heat coagulation and that product of the action of acid on native protein which is generally called acid albumin are certainly different substances.

In dealing with the decomposition products of the proteins those recently described by Skraup are given the same consideration as those which have been thoroughly established and studied, although the evidence of the identity of these products given by Skraup was extremely unsatisfactory, and he has since shown that most of them were mixtures of well-known substances, and are therefore to be no longer considered.

The reader will be surprised to find diaminopropionic acid in the list of protein decomposition products, together with the statement that this is the simplest diamino-acid found in the body. Meyer is cited as authority for this statement, but the author has overlooked the fact that the diaminopropionic acid which was obtained from rabbits Meyer himself had already introduced. Misapplications of quotations are to be found in this book, against two of which the reviewer must strongly protest. On page 297 he says that "Osborne has stated that the globulin precipitation is caused by the hydrogen ions of the water," a view which the reviewer not only never advanced, but considers to be absurd. Again on page 362 he repeats the same statement in connection with the conversion of globulin into insoluble products, which the reviewer showed to be due to the action of acids, but did not attribute to the hydrogen ions of water. On page 372 he makes the reviewer responsible for the statement that the Para-nut contains an albumin, "the lime

and magnesia salts of which crystallize in octahedra." So far as known, the lime or magnesium salts of this protein have never been prepared and probably cannot be crystallized if made.

His description of the properties of the individual proteins closely follows Cohnheim except in the case of the nucleoproteids and the haemoglobins, which are treated more extensively.

Throughout the volume, references are made to the original authorities, and this fact gives the book its chief value, for the entire literature of the subject is discussed, and few papers of consequence have been overlooked. The reader will therefore find this book very helpful in looking up the literature of any of the questions treated.

It is unfortunate that in the first work in the English language on this subject a more critical study of this great mass of undigested material was not undertaken, and an endeavor made to bring the conflicting statements into harmony and to eliminate those already disproved or rendered extremely improbable. As it is, we here have collected together, in addition to the definitely ascertained facts, a large number of very questionable observations and evident blunders which thus acquire an undeserved degree of recognition that will make it difficult to dispose of them for a long time to come.

THOMAS B. OSBORNE.

ON CARBOHYDRATE METABOLISM. By F. W. PAVY, M.D., LL.D., F.R.S.  
Philadelphia: P. Blakiston's Son & Co. Price, \$2.40.

This book contains a course of advanced lectures delivered by Dr Pavy at the University of London in May, 1905. It is largely made up of the personal experiments and opinions of its author. It hardly seems credible that the subject of diabetes could have been treated without reference to Minkowski's work on the extirpation of the pancreas, yet this has been done. Much foreign work has been neglected or misquoted. Dr. Pavy (p. 50) considers that carbohydrate to the extent of 60 per cent. may enter into fixed chemical combination in the proteid molecule. This is an old view, now relegated to the group of fallen theories, since it has been shown that proteid yields sugar in metabolism through a synthetic reconstruction of the broken chains of its constituent amino acids. Dr. Pavy rightly protests that the "acidosis" question in diabetes should not engross the attention in preference to that of sugar. GRAHAM LUSE.

**THE MICROSCOPY OF VEGETABLE FOODS WITH SPECIAL REFERENCE TO THE DETECTION OF ADULTERATION AND THE DIAGNOSIS OF MIXTURES.**  
By ANDREW L. WINTON, PH.D., Chemist of the Connecticut Agricultural Experiment Station and Instructor in the Sheffield Scientific School of Yale University, with the Collaboration of Dr. Josef Moeller, Professor of Pharmacology in the University of Graz. New York: John Wiley and Sons. 1906. Large 8vo, xvi + 701 pages, 589 figures. Cloth, \$7.50.

With the increased interest in every branch of food inspection research in this country, the present work is most timely. There has been no dearth of books by Austrian, French and German pharmacologists on food microscopy, but these have had very limited circulation in this country and have hence been of little aid to the American student. This work is certainly unique in that it is the only book in the English language that covers exclusively and comprehensively the microscopical examination of foods, though the subject has been treated incidentally in several English and American works on food analysis.

Dr. Winton is peculiarly equipped by experience for this work, having spent many years in the field of microscopical research in its special application to foods. He has had the advantage of several periods of close association and coöperative work with that pioneer author and teacher in food microscopy, Dr. Moeller, in his laboratory at Graz. Indeed, in the latest German edition of Moeller's "*Mikroskopie der Nahrungs- und Genussmittelaus dem Pflanzenreiche*," which has recently appeared, Dr. Winton is collaborator.

"The Microscopy of Vegetable Foods" is, however, in no sense a translation of the German work, the arrangement and plan of the two books being entirely different. The American work is, of course, of paramount interest to English and American students and has evidently been planned with special reference to their needs.

Apparatus, reagents and general technical methods are first described, and a brief though comprehensive résumé is given of the histological elements found in foods and of the morphology of the various organs including the flower, fruit and stem. Then follows in considerable detail a systematic treatment of the grains, seeds, legumes, nuts, fruits, vegetables, alkaloidal products, spices and condiments and commercial starches, each subject being developed to show as far as possible the general

plan and function of each particular food product in the plant economy, as well as the morphology and structure of its tissues, and its most characteristic and recognizable features under the microscope from a diagnostic standpoint. Not only are the simple or elemental food products thus treated, but in many cases the commoner compounds or mixtures, such as fruit preserves, table sauces, and condimental cattle and poultry foods are described with reference to the detection of their ingredients.

Most important of all in a practical way is the special attention given throughout to methods for the detection of adulteration. It is especially in the last feature that the book is invaluable to every analyst who has to pass judgment on the purity of foods. In all cases impurities incidental to the commercial preparation of the various food products are thoroughly discussed, as well as adulterants intentionally added, and the same attention is given to the characteristics of the impurities and adulterants as to those of pure foods.

Much of the practical value of such a book as this naturally rests in the character of the cuts, of which there are nearly 600. By far the larger portion of these are from drawings made by the author and collaborator, though cuts have been selected from over 30 other microscopists, making in all a very complete series. Every cut bears the name of its author. From an artistic standpoint these drawings leave little to be desired, but it would seem as if a word of caution should be given as to their limitations and practical use for direct comparison in the examination of actual samples. It should be made plain that most drawings of sections show what would be seen under ideal conditions only, assuming for instance that it were possible to obtain a mechanically perfect section, and that in many cases the student should not expect in the microscopic appearance of the confusing fragments and débris of a powdered specimen the same beautiful arrangement of cells and tissues that he sees in the idealized drawing.

As a guide in diagnosis, one cannot but commend the clever analytical keys to cereals and weed seeds, cruciferous seeds, legumes, umbelliferous fruits and spices devised by the author. These are based on the color, shape or size of the various tissues, fibers, cells or cell contents, and by comparison of the most distinctive differences in structure serve in many cases to classify and group each series in a very systematic manner. It is un-



fortunate that these keys are not always applicable, since many products lack certain elements present in the original material.

Arranged at frequent intervals through the book in connection with the treatment of each special subject are very exhaustive bibliographies, with cross references to a complete general bibliography near the end. The volume closes with a useful glossary of botanical terms.

A word of commendation should be spoken on the attractive form and appearance of the book. Of necessity it is large but not cumbersome, is excellently bound and printed, and furnishes one of the best examples of modern book-making in the class of text-books.

ALBERT E. LEACH.

NOTES ON ELECTROCHEMISTRY. By F. G. WIECHMANN, PH.D. New York: McGraw Publishing Co. 1906.

Within a compass of less than 150 octavo pages the author gives an abundance of data relating to electrochemistry, helpful to students and practical men alike. The book is not a text-book in the ordinary sense of the word, but a compilation of facts to which one may often feel inclined to turn to refresh one's mind upon electrochemical topics.

E. F. S.

A SYSTEMATIC COURSE OF QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC AND ORGANIC SUBSTANCES WITH EXPLANATORY NOTES. BY HENRY W. SCHIMPF, PH.G., M.D., Professor of Analytical Chemistry in the Brooklyn College of Pharmacy. New York: John Wiley & Sons. 1906. vii + 156 pp. Price, \$1.25.

This book is an epitome of the principal reactions in analytical chemistry, prepared for students in pharmacy. As the time which can be devoted to chemistry in a course of pharmacy is short, the book is correspondingly brief. It contains, however, the gist of analytical chemistry, both inorganic and organic. Part I, devotes 16 pages to "Definitions and General Considerations." Part II gives 63 pages to inorganic qualitative analysis, but includes the organic acids. The observation that "students should prepare their own reagents and not be kept in the dark as to their strength" is good for small classes; the caution regarding impurities in reagents is wise. The last 65 pages of the book are on organic qualitative analysis, and this portion is fairly comprehensive. Sugars, alkaloids, poisons, urine, as well as a large share of the more common synthetic medicines, are included.

Typographical errors are rare, and the make-up of the book is good.

JAS. LEWIS HOWE.

**METALLURGICAL CALCULATIONS** By JOSEPH W. RICHARDS, A.C., PH.D.  
PART I. INTRODUCTION, CHEMICAL AND THERMAL PRINCIPLES,  
PROBLEMS IN COMBUSTION. New York McGraw Publishing Com-  
pany 1906 Price, \$2.00.

This book contains a reprint of a series of papers published in "Electrochemical and Metallurgical Industry" from March, 1905 to March, 1906, to which have been added many problems for practice. Other papers yet to appear in the same journal are expected to make up a second and a third part of the completed work.

Chapter I fully explains the use of chemical equations for such computations of weights, and of volumes in case of gases, as may be required in metallurgical operations. The second chapter treats of the applications of thermochemistry, and the third chapter explains and well illustrates the applications of thermochemical data. Chapter IV treats of the thermochemistry of high temperatures, and chapter V, of specific heats, heats absorbed in fusion, and other related matters. The titles of the three following chapters are, "Artificial Furnace Gases," "Chimney Draft and Forced Draft," and "Conduction and Radiation of Heat." There is an appendix containing twenty-three problems in addition to the twenty-four given in the text. Chapters II, IV and V contain copious tables of data. The metallurgical master will need this harmonious collection of the physical data of his art, and the metallurgist who is not yet a master will find the clear teachings of this book an indispensable guide to the understanding of the scientific principles on which his art is founded, and by the knowledge of which only can it be intelligently advanced.

EDWARD W. MORLEY.

**A HANDBOOK FOR CANE-SUGAR MANUFACTURERS AND THEIR CHEMISTS.**  
By GUILFORD L. SPENCER, D.Sc., formerly Chief of Sugar Laboratory  
U. S. Department of Agriculture, Chief Magnolia Plantation, Chaparra  
Sugar Co., Cuban-American Sugar Co., Nicaragua Sugar Estates, Ltd.,  
etc. 16mo. viii + 331 pp. 52 illustrations, morocco. New York :  
John Wiley & Sons. London : Chapman & Hall, Ltd. 1906. Price,  
\$3 00.

This book is the fourth edition of the same work by this author,

and is greatly enlarged both in its general scope and the scientific data presented.

The first fifty pages are devoted to the manufacture of cane sugar from the sugar-cane, which is given in compact form, covering the methods generally used, also appearing for the first time in an English publication combined with the chemical control of sugar houses. This brief treatise is very complete and reliable, covering both general and special methods.

Article No. 31, on the composition of sugar-cane molasses, by Dr. C. A. Browne, Jr., chemist of the Louisiana Sugar Experiment Station, Audubon Park, New Orleans, La., is a very clever and useful treatment of this subject, and the most complete report on this subject published in technical form.

The properties of the sugar in the cane, and methods of analysis, are concisely given and in addition the general analytical work on sugar estates is included.

The remarks on the control of the sugar house work are given very fully and many valuable suggestions as to the scope of the chemist's work are clearly brought out.

The concluding chapters refer to analyses and examinations of materials used in sugar manufacture and in the sugar house, with a collection of useful reference tables, and the properties of the carbohydrates completing the volume.

The edition is a marked improvement over former editions of this work (which were highly appreciated by sugar house chemists and manufacturers) and the author has carefully kept pace with the advancements in this line.

Those desiring a concise and ready reference treatise on the manufacture of sugar and the chemical control of sugar houses will find this work worthy of careful attention.

R. E. BLOUIN.

JAHREBUCH DES VEREINS DER SPIRITUS-FABRIKANTEN IN DEUTSCHLAND.  
Sechster band, von DR. G. HEINZELMANN. xiii + 499 pp. Berlin :  
Paul Parey, 1906.

The annual report of the Society for the Manufacture of Alcohol in Germany comes at a very opportune moment. The people of this country are much interested at the present time in the subject of free alcohol in the arts, and there is a woful lack of technical knowledge among our people respecting both the raw materials from which alcohol may be made, and the methods of making

it. The report is prefaced by a discussion of its chief characteristics by the editor, Dr. Delbrück, of the German Brewing School of Berlin. The chemical and technical part consists of a discussion of the improvements in saccharimetric measurements; of the determination of sulphur in fuels; of the uses of ether and alcohol mixtures for illumination; the corrosion of metals by denatured alcohol; the ash content of yeasts; the improvement of the taste of lager beer distillates; various improvements in analytical processes relating to distillation; the manufacture of vinegar; and the manufacture of starch from different substances.

A special chapter is devoted to the methods of determining nitrogen and their application in the estimation of the albumen content of barley, the protein content of the harvest of 1905 and the relations existing between the protein content of barley and the general extract thereof. An interesting chapter also is that relating to the drying of potatoes for technical purposes.

The report also contains the Proceedings of the Fifty-fourth annual meeting of the Society. Reference is made to the celebration of Dr. Kühn's eightieth birthday, and to the unveiling of the Maercker monument. The appendix gives statistics pertaining to the production of spirits for the year ended September 30, 1905.

There is no space here to mention all the interesting topics in this volume. It is to be commended to all those chemists who are taking particular interest in the problem of denatured alcohol in the arts and allied problems.

H. W. WILEY.

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CHEMISTRY OF THE MATERIALS OF ENGINEERING. By A. Humboldt Lexton. Revised and enlarged edition. London: Technical Pub. Co. 1906. 348 pp. 5/.

PRACTICE OF PHARMACY. By J. B. Remington. London: Lippincott. 1906. 1504 pp. 25/.

ÜBER DIE BEDEUTUNG DER ELEKTRONENTHEORIE FÜR DIE CHEMIE. By Otto Sakur. Halle: W. Knapp. 1905. 21 pp. Mark 1.-

TRAITÉ DE CHIMIE MINÉRALE. By H. Moissan. Vol. 5. Paris: Masson et Cie. 12+972+88 pp. 34 fr.

DIE BEZIEHUNG ZWISCHEN FLUORESCENZ UND CHEMISCHER KONSTRUKTION. By Hugo Kauffmann. Stuttgart: F. Enke. 1906. 102 pp. Marks 2.40

CHEMIE DER ORGANISCHEN FARBSTOFFE. By Rudolf Nietzki. Fifth edition. Berlin: J. Springer. 1906 15+362 pp. Marks 8.-

SYNOPSIS OF MATRICULATION CHEMISTRY. By W. Briggs. London: Clive. 1906. 98 pp. 1/6.

METALLURGICAL CALCULATIONS. PART I, INTRODUCTION, CHEMICAL AND THERMAL PRINCIPLES, PROBLEMS IN COMBUSTION. By Joseph W. Richards. New York: McGraw Publishing Co. 1906. 11+208 pp. \$2.00.

NOTES ON ELECTROCHEMISTRY. By Ferdinand Gerhard. Wiechmann. New York: McGraw Publishing Co. 1906. 6+145 pp. \$2.00.

CONTRIBUTION A L'ÉTUDE DU DOSAGE DE LA MORPHINE DANS L'OPIMUM. (THÈSE). By L. Picard. Lyons: Rey et Cie. 124 pp. 2 fr. 25.

LEÇONS DE CHIMIE. 2<sup>e</sup> ET 3<sup>e</sup> ANNÉES. By Tanqueray et P. Poiré. Paris: Ch. Delagrave. 3 fr. 50.

TREATISE ON PHARMACY FOR STUDENTS. By C. Caspari. Third edition. London: H. Kimpton. 1906. 21/.

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GAS ENGINEERS INSTITUTION TRANSACTIONS, 1905. London: Spon & Chamberlain. 1906. 10/6.

HANDBUCH DER BAUMWOLLINDUSTRIE. By E. Frank. Berlin: Verlag f. Textilindustrie. 1906. Marks 5.-

BETRIEBSVORSCHRIFTEN FÜR DROGEN- U. GIFTHANDLUNGEN IN PREUSSEN. By E. Urban. Berlin: J. Springer. 1906. Marks 2.-

THEORIEN DER CHEMIE. By S. Arrhenius. Leipzig: Akadem. Verlags-Gesellschaft. 1906. Marks 7.-

DIE CHEMISCHE REICHSANSTALT. By W. Ostwald. Leipzig: Akadem. Verlags-Gesellschaft. 1906. Marks 1.-

EINFÜHRUNG IN DIE CHEMIE. By O. Stöckenius und O. Krüger. Leipzig: Renger. 1906. Marks 1.20.

DIE CHEMISCHE DÜNGERINDUSTRIE. By L. Schucht. Braunschweig: F. Vieweg. 1906. Marks 5.-

LEHRBUCH DER ANORGANISCHEN CHEMIE. By V. von Richter. Eleventh edition. Bearb. von Prof. Klinger. Bonn: F. Cohen. 1906. 12+534 pp. Marks 10.-

ALLGEMEINE UND PHYSIOLOGISCHE CHEMIE DER FETTE FÜR CHEMIKER, MEDIZINER UND INDUSTRIELLE. By F. Ulzer and J. Klimont. Berlin: J. Springer. 1906. 11+317 pp. Marks 8.-

# THE JOURNAL

OF THE

# American Chemical Society

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## THE ELECTRIC VACUUM FURNACE.

BY WILLIAM C. ARSEF.

Received June 4, 1906.

I. *Historical*.—Previous work *in vacuo* at high temperatures has been confined to experiments with quartz and porcelain tubes.

Schuller distilled and sublimed various elements and compounds in evacuated quartz vessels. The boiling-points of many metals have been determined in evacuated porcelain tubes by Kahlbaum, Roth, Siedler, Krafft, Bergfeld, Lehmann and others. In all cases, however, the vessels were subjected to external atmospheric pressure, and the scope of the experiments was limited by the temperature at which they collapsed. Porcelain collapsed between  $1400^{\circ}$  and  $1500^{\circ}$ , and quartz at somewhat higher temperatures. Moreover, certain metals and other substances which attack quartz and porcelain could not be investigated.

In the electric vacuum furnace described below, the attainable temperature is limited only by the vaporization of carbon, and crucibles of any material suitable for a particular experiment may be used.

II. *Description*.—The vacuum furnace is a special type of resistance furnace enclosed in a vacuum chamber, with means for continuous cooling of the parts liable to be injured by excessive heating, and so designed that the effect of heat on any substance or the course of any reaction may be studied up to the vaporizing point of carbon, the substance in the crucible being always visible through a window.

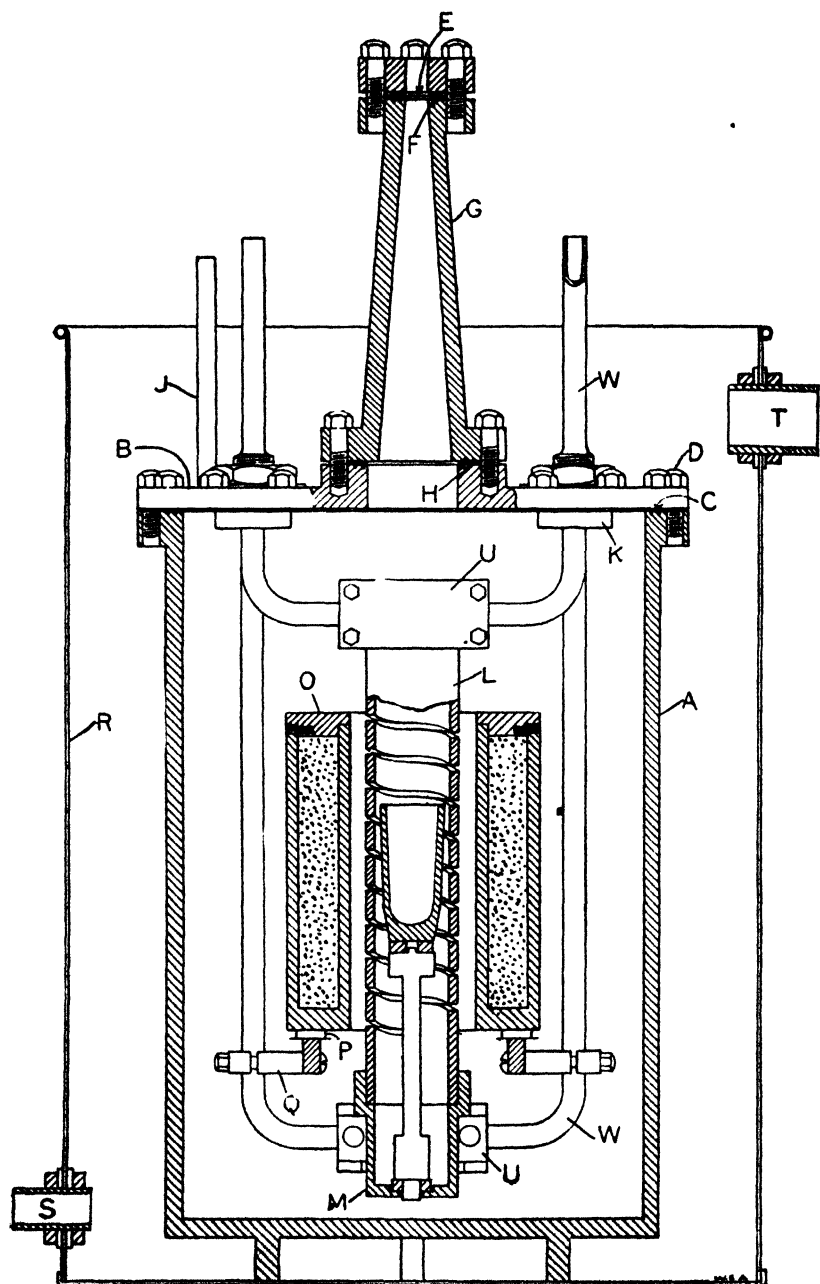


Fig. 1. Sectional elevation of electric vacuum furnace.

A calibration of the furnace to determine the relation of the temperature to the energy makes possible the accurate control of the temperature. The advantages of a vacuum for protecting the heater and the substance being heated are obvious.

It consists of an air-tight metal vessel with tubular electrodes entering the cover. These electrodes are provided with clamps which hold the heater in place and make contact between it and the electrodes. The radiation screen which surrounds the heater to diminish the radiation loss is also held in place by supports attached to the electrodes. The metal vessel stands in a can which serves as a water jacket. When the furnace is running, a constant flow of water is maintained through the water jacket and through the tubular electrodes.

The construction will be better understood from Fig. 1, which is a sectional elevation through the center. The chamber (A) and cover (B) are castings of gun-metal turned true at the joint. A lead gasket (C),  $\frac{1}{16}$  inch thick, forms an air-tight joint when the cover is fastened down with the cap-screws (D). The first time the furnace is assembled, the tightening of the screws forces the lead into the annular grooves of the chamber and cover. The ridges thus formed in the lead washer, and suitable reference marks on the cover and chamber, make it possible to replace the parts in the same position after opening the furnace for cleaning or repairs. Leakage, due to porosity of the casting, is prevented by applying a thin coat of solder all over the inner and outer surfaces of the chamber and cover, after turning to dimensions. The chamber has four legs to permit the flow of water underneath. The tube (J), through which the air is exhausted, is soldered into the cover.

The window (E) is a disc of clear white mica about 0.005 inch thick, clamped between two lead washers (F) by means of a brass cap and four cap-screws. The brass surfaces touching the lead washers have annular grooves into which the lead is forced by the pressure. The window tube (G) is of gun-metal and is fastened to the cover by six cap-screws, the joint being made tight by a lead washer (H).

The electrodes (W) are formed of brass tubing bent into shape. The threaded brass bushings (K, K) which constitute parts of the electrode joints, are soldered to the electrode tubes.



The construction of an electrode joint is shown in detail in Fig. 2. Two lead washers ( $W_1$ ,  $W_2$ ), separated by a mica washer, are interposed between the cover and the flange of the bushing. The bushing is insulated from the cover and the upper lead washer ( $W_2$ ) by the fibre sleeve ( $S$ ), and the nut ( $N$ ) is insulated from the cover by the fibre washer ( $F$ ). The fibre parts are impregnated with paraffin to make them waterproof. By tightening the nut ( $N$ ), a perfectly tight, electrically insulated joint is obtained. The heater-clamps ( $U$ ,  $U$ ), Fig. 1, are of copper.

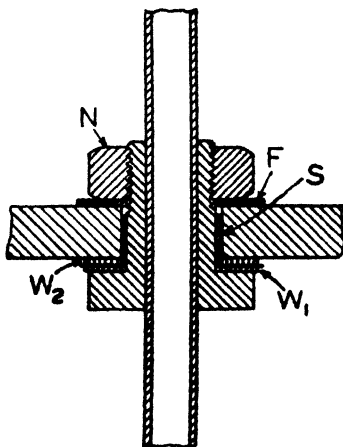


Fig. 2. Section of electrode joint

The heater ( $L$ ) is a helix of conducting material such as carbon or graphite. Artificial graphite is preferred for high temperature work because of its freedom from impurities. Metallic heaters can be used for some purposes and have certain advantages, one of which is the inability to absorb air when cold. A heater is made by sawing a slot in a hollow graphite cylinder. Its dimensions and the number of turns are so related that at the highest temperature reached the potential difference across the heater shall not be much more than 50 volts, in order to avoid excessive Edison effect and the tendency to arc across to the screen. Good results have been obtained with a heater 2 inches outside diameter,  $1\frac{5}{8}$  inches inside diameter, and having ten turns in a length of  $7\frac{1}{2}$  inches. The graphite cup ( $M$ ) holds the lava insulating ring on which the crucible support rests. The proximity of this ring to the cold bottom of the furnace prevents it from fusing or being made conducting by heat.

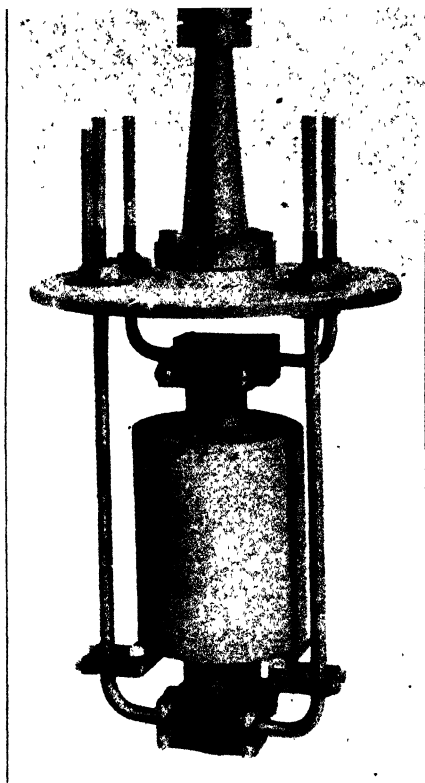


Fig. 3 Electric vacuum furnace





The radiation screen (*O*) is a double-walled cylindrical box of Acheson graphite, filled with graphite powder. Its purpose is to minimize loss of heat by radiation. Owing to the low thermal conductivity of the powdered graphite, the inner wall of the screen becomes nearly as hot as the heater, and then the rate of radiation from the heater to the screen, which depends upon the temperature difference, becomes very small, and equal to the rate at which heat is conducted away through the graphite powder. It was found that with the use of the screen, the melting-point of platinum could be reached with but one-fourth of the energy necessary without it. The screen is supported by the copper arms (*Q*) from which it is insulated by the lava buttons (*P*).

The water jacket (*R*) is a galvanized iron tank provided with an inlet (*S*) and outlet (*T*).

Fig. 3 shows the interior parts of the furnace raised out of the chamber. In Fig. 4 are shown two vacuum furnaces which have had almost constant use for two years. These have no window tubes, but the windows are fastened directly to the covers of the furnaces.

III. *Crucibles and Crucible Supports*.—The choice of material for crucibles is determined by the nature of the substance to be heated and the temperature reached. Graphite crucibles are used when the substance to be heated is not acted upon by carbon, and are conveniently made from solid rods of Acheson graphite.

Magnesia crucibles are frequently used for fusing metals and preparing alloys when the temperature to be reached does not exceed  $1650^{\circ}$ . These crucibles are made by strongly compressing in a steel mold by means of a hydraulic press, a mixture of finely powdered and sifted magnesia with a suitable binder. A porcelain kiln was used for firing the magnesia before using and for baking the crucibles, the temperature attained being about  $1350^{\circ}\text{C}$ . Crucibles made from magnesia fired at a lower temperature are very liable to crack, owing to the great shrinkage which they undergo between  $1200^{\circ}$  and  $1600^{\circ}$ .

Other metallic oxides have been found to be more suitable than magnesium oxide as crucible material. In many cases oxide crucibles must be separated from the graphite support by a refractory metal cap, to prevent reduction at the contact surface.

Crucibles of iron, copper, fire-clay, porcelain and thorium oxide have been used for special purposes, the latter substance with-

standing a higher temperature than anything else tried except graphite.

In Fig. 1, a crucible and graphite support with a metal cap are shown partly in section.

IV. *Accessory Apparatus. Vacuum Pump.*—A double-cylinder Geryk oil-pump is used with the cylinders in series. It gives a good vacuum in the furnace fifteen minutes after starting. The pump is connected to a brass main-tube having soldered branches to which the furnace, gauge, and air inlet valve are connected by means of heavy rubber pressure-tubing. The joints are made tight by brass sleeves, the ends of which are filled with a wax mixture. Brass stop-cocks were first used, but were later replaced by mercury-seal glass cocks which did not leak.

*Vacuum Gauge.*—A closed mercury gauge of the manometer type was used at first, but it gradually became soiled and an uncertain capillarity error was introduced, which made it unreliable for accurate measurements. To avoid this, the gauge is now connected through a tube containing glass wool and potassium bicarbonate crystals to retain dust and acid vapors, with an auxiliary tube containing a drying agent.

*Electrical Apparatus.*—The current is furnished by a single-phase alternator in connection with a step-down transformer. Regulation of the current is effected by means of rheostats in the generator field circuit. The measuring instruments are of the Thomson inclined-coil type. The voltage is measured directly, the current being first reduced by a current transformer.

V. *Operating Conditions. Vacuum.*—When all joints have been properly tightened, the pressure can be reduced to a fraction of a millimeter of mercury. If leaks are suspected, the furnace is closed, the jacket is filled with water and compressed air is forced into the chamber. Leaks are shown by air-bubbles. If due to defects in the casting, they can be repaired by soldering, or if not too large, by painting with pyroxylin lacquer. Leaks at the electrode-joints may occur when a new furnace is first assembled, but these disappear when the nuts are tightened sufficiently. The vacuum becomes somewhat poorer as the temperature in the furnace rises, especially with a new heater and screen, owing to the escape of gases from the graphite or from the substance which is being heated, but on maintaining the temperature at a definite point, the vacuum finally improves up to the starting value.

A high vacuum can be maintained even at the vaporizing point of graphite.

*Description of Run.*—The crucible is placed on the support and centered so that it does not touch the heater, the window tube is then fastened down, the washer and contact surfaces having been first carefully cleaned. When a good vacuum has been established the current is switched on and the water allowed to flow at such a rate through the jacket that it comes out barely warm, the water-level being above the window joint. Water is also passed through the electrode tubes, the outflow being allowed to play against the side of the window tube. In most cases the current should be raised gradually, so that the behavior of the heated substance can be followed.

The substance or article being heated is observed through the mica window, colored glass being used to protect the eyes at temperatures above  $1100^{\circ}\text{C}$ . At  $2500^{\circ}\text{C}$ . and above, three or more thicknesses of blue glass are necessary to make it possible to distinguish the outlines of the substance, because of the intensity of the light.

When the desired result has been obtained, the circuit is opened. From one to three hours are allowed for cooling, according to the temperature reached, then the water is let out of the jacket, air is admitted to the furnace, the window tube is unfastened and the crucible is removed.

VI. *Temperature Estimation.*—Owing to the small total heat capacity of the heater and screen, the temperature very soon reaches a constant value for each value of the energy used, and it is therefore possible to calibrate the furnace so that the relation of temperature to energy is known.

For this purpose the melting-points of copper and platinum were taken as fixed points, and the amounts of energy required to maintain these temperatures continuously were determined, the procedure being as follows:

Some pieces of electrolytic copper were fused in a graphite crucible so as to obtain oxygen-free copper with the melting-point  $1084^{\circ}$  (Holborn and Day). The current and voltage were read just when fusion began. The current was then diminished until the copper solidified and then gradually raised about one ampere every five minutes until the copper melted again. This

procedure was repeated a number of times, and the product of the lowest average values of the current and voltage was taken as the energy corresponding to the melting-point of the copper. Fusion of the globule was characterized by the appearance of a dark spot on top, this being the only part of the globule which reflected no light vertically upward. Freezing of the globule was accompanied by the disappearance of the dark spot when the copper crystallized and the surface was no longer smooth.

A piece of chemically pure platinum wire was heated in a small cup of thorium oxide inside of a graphite crucible. The current was very gradually raised as the melting-point was approached, this having been approximately determined previously. The readings were taken while beads of melted platinum were slowly forming on the wire. The melting-point of platinum was taken as  $1780^{\circ}\text{C}$ . (Le Chatelier).<sup>1</sup>

To find a mathematical relation between the energy and temperature the observed values were tried in various well-known formulae, and it became evident that only an exponential equation would answer.

The expression chosen was  $y^n = ax$ , in which  $y$  represents the temperature of the crucible above that of the room,  $x$  is the energy in kilovolt-amperes, and  $n$  and  $a$  are constants. For convenience the equation was used in the form  $(y-20)^n = ax$ , or  $n \log (y-20) = \log a + \log x$  in which  $y$  is the actual temperature centigrade of a crucible at the middle of the heater, the average temperature of the water in the jacket at the start,  $20^{\circ}$ , being taken as the temperature of the surroundings.

The average values found by the experiments described were:

Temperature ( $20^{\circ}$ )	Kilo-volt-amperes. (0 0)
1084°	1.909
1780	4.953

From these values the constants were calculated:

$$\begin{aligned} n &= 1.895 \\ \log a &= 5.4552 \\ a &= 285200 \end{aligned}$$

<sup>1</sup> Recent work gives the melting-point as  $1710^{\circ}$  by the thermoelectric couple (Harker: Chem. News, 91, 250 (1905); Holborn and Henning: Ber. Berl. Akad. 1905, p. 316) and  $1745^{\circ}$  by optical methods. Nernst and Wartenberg: Verh. deut. phys. Ges. 1906, p. 48.—EDITOR.

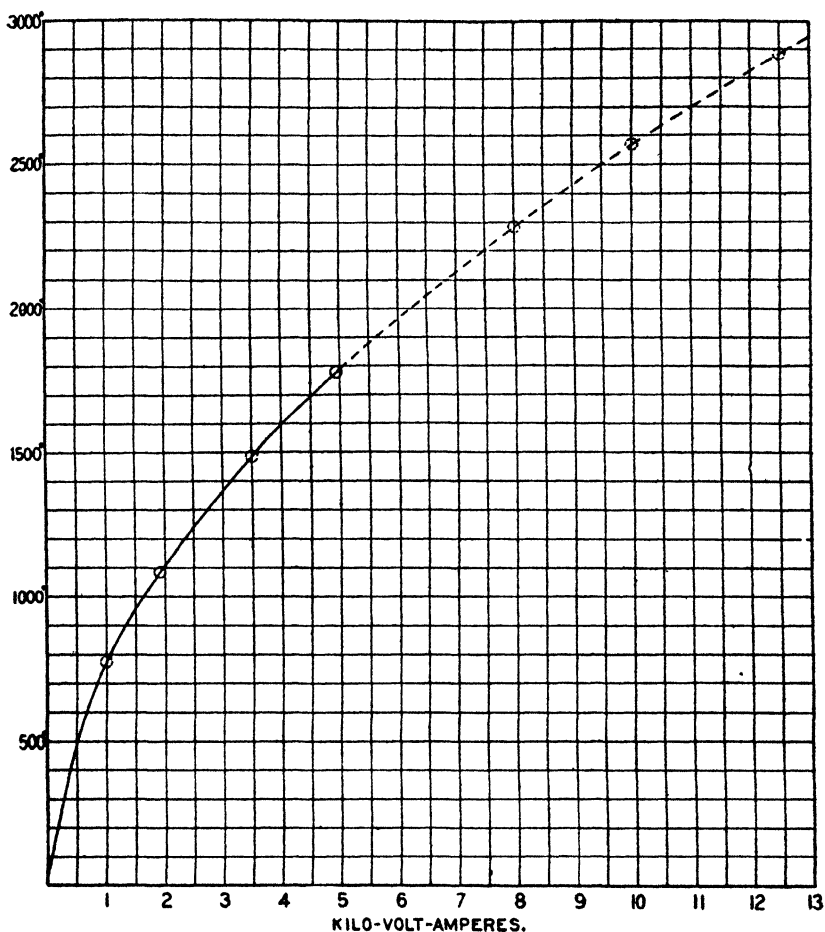


Fig. 5. Curve showing relation of temperature to energy in electric vacuum furnace.

The curve (Fig. 5) was plotted from the results obtained, the dotted portion being continued through extrapolated points calculated from the equation.

*Accuracy of Calibration.*—The principal source of error was the slight variation of the generator voltage. The variation at the melting-point of platinum was 4.915 to 4.992 K. V. A., corresponding to an uncertainty of  $25^{\circ}$  in temperature.

If the equation holds at higher temperatures, the error thus introduced into the constants will make measurements in the neighborhood of  $3000^{\circ}$  uncertain by  $50^{\circ}$ .



I hope later to check these calculations by an optical pyrometer, which should give accurate results, since any substance heated in the furnace, being enclosed by walls at the same temperature, will radiate like a black body.

The calibration up to  $2000^{\circ}$  is at least sufficiently accurate for practical purposes. In one experiment, the furnace was running constantly day and night for ninety hours, keeping the temperature very close to  $1800^{\circ}$ .

(No correction was made for the small current which flows through the water between the electrodes.)

VII. *Edison Effect*.<sup>1</sup>—In one of the first forms of the furnace, the radiation screen was supported by the lower clamp, and the crucible support was also in electrical contact with the clamp, as

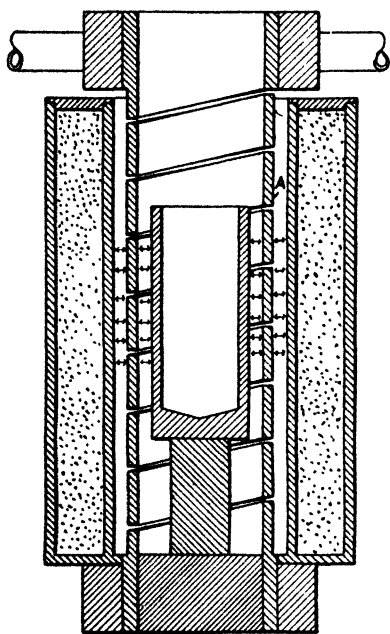


Fig. 6. Arrangement of furnace No. 1, giving single-ring "Edison effect."

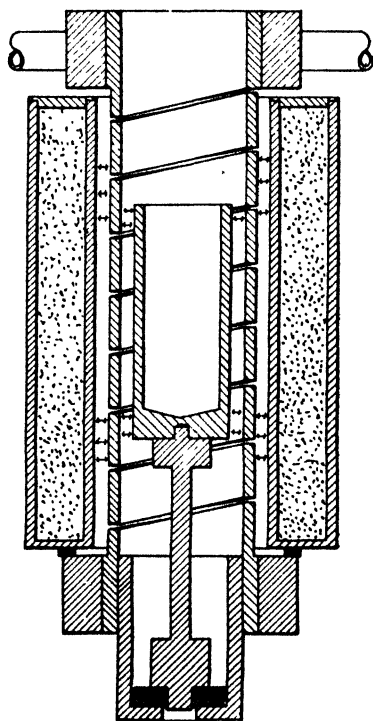


Fig. 7. Arrangement of furnace No. 1, giving double-ring "Edison effect."

shown in Fig. 6, the need for further insulation being then unknown. With such an arrangement a rise of current and a

<sup>1</sup> T. A. Edison, 1884. Preece: *Pr. Roy. Soc.* 38, 219 (1885); Fleming: *Pr. Roy. Soc.* 47, 118 (1889).

simultaneous fall of voltage was observed as the temperature approached  $2000^{\circ}\text{C}$ . and an arc would soon start at the point *A*, Fig. 6. This was found, by the arrangement shown in Fig. 8,

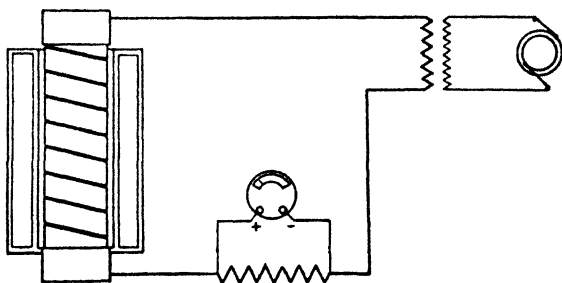


Fig. 8. Connections for showing "Edison effect"

to be due to a discharge taking place across the space between the heater and the screen. The heater being at a slightly higher temperature than the inside of the screen, an excess of current flowed across the space in such a direction that the heater was negative, and amounted to two amperes at times. The arrangement was first calibrated by passing a direct current through the shunt and meter in parallel, and noting the reading of the meter for each value of the current.

In a later form of the furnace, with the screen and crucible support both completely insulated from the heater (Fig. 7), a similar variation was observed but of much smaller magnitude, and there was now no tendency to arc across. The relative variation in the two cases is shown in Fig. 9. The paths of the discharge in the two cases is shown by the arrows in Figs. 6 and 7, and by the black coatings found on the heater, screen and crucible after a high temperature run.

The ease with which ionization takes place at high temperatures is thus shown in a striking manner.

In Fig. 10, *b* and *c* show the deposit produced on the heater and crucible at high temperatures, with the arrangement shown in Fig. 6. The location of the arc is shown in *a*, Fig. 10, the black deposit being brushed off to show clearly the disintegration which has taken place. Fig. 11 shows two crucibles with the double-ring deposit obtained with the furnace arranged as in Fig. 1 or Fig. 7.

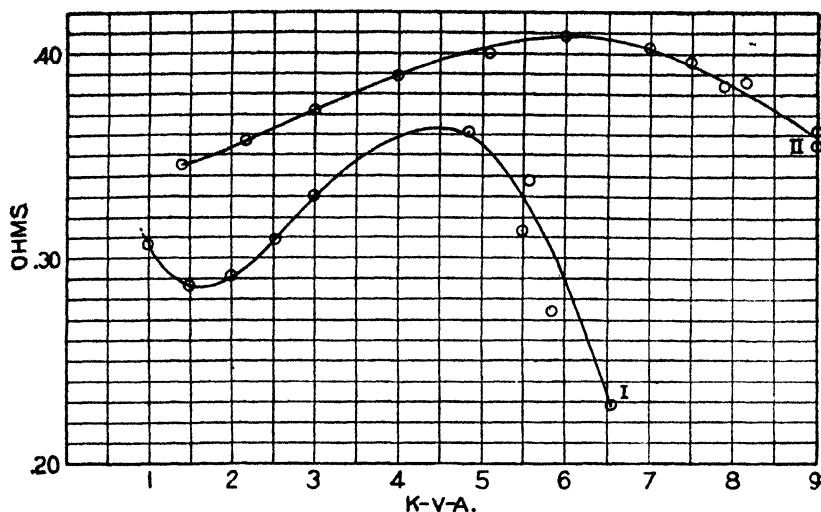


Fig. 9. Curves showing variation of resistance of heaters with temperature, for two arrangements of furnace shown in Figs. 6 and 7

To pass a discharge through a rarefied gas as in a "vacuum tube" requires a certain fall of potential, mainly at the cathode. During the passage of the discharge, the cathode is disintegrated, the detached particles moving normally from the surface of the cathode, and depositing on the nearest surface.

It is well-known that the cathode fall diminishes as the temperature of the cathode is raised.<sup>1</sup> When the cathode becomes hot enough to have an appreciable vapor-pressure, the glow discharge becomes an arc.<sup>2</sup>

We therefore have in the furnace a complete analogy to the phenomena in a vacuum tube. The points between which the small arrows are placed become alternately anode and cathode to the alternating current, which leaks between them through the ionized gas, so that the erosion takes place on both surfaces. The gradual apparent lowering of the resistance of the heater with rise of temperature shown by the curves in Fig. 9, is due to the increasing leakage of current across the space where the arrows are. With the furnace arranged as in Fig. 7 there are two discharges in series. Between the two rings there was not a great enough potential difference to maintain two discharges.

Two explanations are possible for the presence of the rings.

<sup>1</sup> Cunningham: Phil. Mag. 9, 193.

<sup>2</sup> Hittorf: Ann. Physik. 21, 90 (1884).

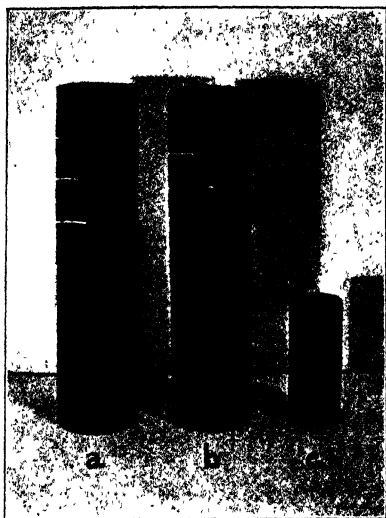


Fig 10. Two heaters and crucible showing single-ring "Edison effect," and arc spot.

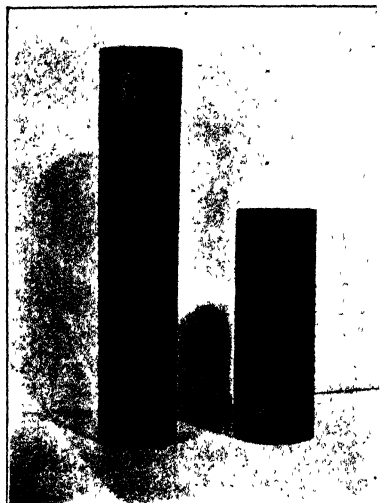


Fig 11 Two crucibles showing double-ring "Edison effect "

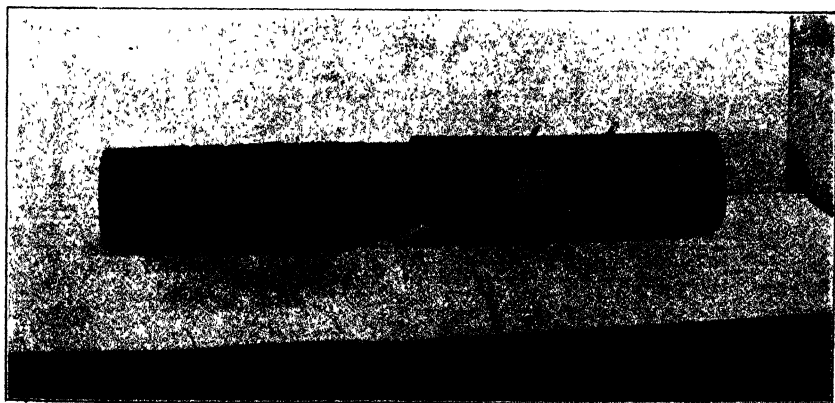


Fig. 12. Graphite heater after high temperature run.



(1) A certain minimum potential difference is required to produce a discharge at a given temperature, just as there is for an arc. This minimum is then just half that across the unblackened space on the heater between the rings, and lies between 10 and 15 volts.

(2) The resistance along the path taken by the discharge may be less than the resistance of the heater between the rings.

The second explanation seems inadequate, as it does not account for the complete absence of deposit between the rings. I consider the first explanation more satisfactory.

In the type of furnace shown in Fig. 1 the Edison effect is much reduced by using a heater of lower resistance, so that a lower voltage is required to reach a given temperature, and by making the space between the heater and screen wider. Both the screen and the crucible support are insulated from the heater. The black rings of deposit are now produced only at the highest temperatures (2500° to 3000°).

VIII. *Applications and Results.*—The furnace is especially useful for the fusion or heating of substances at temperatures beyond the range of the ordinary gas-furnace but which cannot be conveniently handled in the arc-furnace because of the excessively high and unmanageable temperature and the presence of carbon vapor. The temperature can be kept constant within less than 25° for any length of time. It makes many experiments possible at high temperatures in the absence of chemically active gases.

Above 2200° work is somewhat restricted by the lack of a crucible material which does not fuse or vaporize, or is not attacked by carbon or the substance to be heated.

Metals obtainable only in the form of a powder containing impurities can be brought into a pure compact state by fusion *in vacuo*, as the non-volatile impurities form a separate layer, and the volatile ones can pass off. Other substances which cannot be heated in air without oxidizing can be fused *in vacuo* without difficulty, unless they vaporize below their melting-points. Aluminum oxide, platinum and other refractory metals have been fused. Magnesium oxide, iron, silicon and aluminum have been vaporized.

Alloys of exact composition can easily be prepared by fusing

their components together. In this way a number of iron alloys have been made.

Chemical reactions, syntheses and reductions can be carried on with great facility under direct observation. Gas-producing reactions can be followed closely by means of the manometer, which shows the temperature at which the reaction begins, and the point at which the reaction is over.

The calibration of an optical pyrometer could be easily performed by comparing it with an electrical resistance pyrometer or a thermocouple heated in the furnace, since any substance heated in the furnace, being enclosed by walls at the same temperature, will give "black body" radiation.

Melting-points of metals, compounds, fire-brick, and other refractory substances can be determined within a few degrees by reference to the calibration curve of the furnace, and still greater accuracy could be obtained with an optical pyrometer.

Substances could be distilled for purification or separation. Magnesium, zinc and cadmium have been thus distilled.

IX. *Vaporization of Graphite, and Life of Heaters.*--At high temperatures the middle of the graphite heater slowly vaporizes, and the sublimed graphite condenses on the colder parts of the heater and radiation screen. Finally the heat tends to become more localized at some thin spot, which rapidly wastes away until a break occurs and an arc starts. This point is indicated by a sudden *drop* in voltage, because the arc so extends itself that one or more turns are short-circuited.

Fig. 12 shows a broken heater with the partly loosened skin of sublimed graphite. This sublimed graphite has an almost silvery whiteness, and under a low-power microscope shows a botryoidal surface.

The average life of a heater at different temperatures is shown by the following table:

Temp.	Life	These results are for hand-sawed heaters. Machine-cut heaters being more uniform will probably have a somewhat longer life.
2500	9 hours.	
2700	3¼ "	
2900	2 "	
3000	1 "	
3100	¾ "	

Since carbon vaporizes from the anode of a carbon arc at about 3700° C., at atmospheric pressure, it is to be expected that *in*

*vacuo* it would vaporize at a much lower temperature. It is therefore very probable that the temperature measurements calculated from the extrapolated part of the curve are fairly accurate, and not overestimated, as had been feared.

In this connection it is of interest to note that Sir Wm. Crookes<sup>1</sup> has calculated from certain assumptions that carbon has zero vapor pressure at 3000° Abs., or approximately 2700°, which is about the temperature (estimated from the calibration curve) at which a more rapid wasting of the heater becomes noticeable.

X. *Conclusion.*—I believe that this furnace opens up a wide field for investigation of high temperature phenomena under exact and easily controlled conditions, and hope that eventually it will enable us to become familiar with the properties of substances up to extremely high temperatures.

I expect soon to be able to give the results of a number of interesting investigations which are now in progress.

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SCHENECTADY, N. Y.

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## ELECTRIC SMELTING AT SAULT STE. MARIE, ONTARIO.<sup>2</sup>

BY E. HAANEL.

Received June 30, 1906.

### INTRODUCTION.

THE disability under which the middle provinces of Canada are placed as regards the upbuilding of an iron and steel industry on account of the necessity of importing the required metallurgical coke either from the United States or the extreme east or west of Canada engaged my attention shortly after assuming the duties of my present position. Considering the fact that the provinces of Ontario and Quebec are supplied with extensive deposits of iron ore and water-powers, the utilization of these water-powers in the production of electric energy in substitution of the energy resulting from the combustion of carbon in blast-furnaces suggested itself as a possible solution of the problem of economically producing pig iron without the use of metallurgical fuel.

Fortunately, the necessity of profitably employing the electric

<sup>1</sup> Pr. Roy. Soc. A 76, 458 (1905).

<sup>2</sup> An address delivered at Ithaca, N. Y., before the American Chemical Society, Saturday, June 30, 1906.

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plants erected in different parts on the Continent, especially in France, for the production of carbide, which had to be closed down as unprofitable, furnished the incentive to invent methods for applying electric energy; first, to the production of the different ferros, and subsequently to the production of pig iron and steel.

In the solution of the problem of applying electric energy to the extraction of metals from their ores Captain Stassano, in Italy, and Héroult and Keller, in France, have rendered conspicuous service. The description of the experiments made by them attracted wide attention, for it was at once seen that if by the electric process pig iron could be economically produced, such countries as Brazil, Chile, Sweden, Norway, Finland and Canada, all rich in iron ore deposits and the necessary fluxes and possessing extensive water-powers, but lacking metallurgical fuel, would be able to render themselves independent of outside sources by employing the electrothermic process for the manufacture of their iron and steel.

It was with a view of ascertaining the practicability of introducing electric smelting into Canada that the honorable Mr. Sifton, then Minister of the Interior, appointed a Commission to investigate this subject. My instructions were: To proceed to Europe for the purpose of investigating and reporting upon the different electrothermic processes employed in the smelting of iron ores and the making of the different classes of steel, now in operation or in process of development, in Italy, France and Sweden.

The special object of this investigation was the ascertainment of all facts in connection with these processes, which were necessary for determining the cost of one ton of product, the quality of the product, and cost of machinery employed and such other facts as were required for the formation of a judgment regarding the feasibility of introducing successfully in Canada electrothermic processes for the production of iron and steel.

I was directed to avail myself of all means necessary to obtain, as far as practicable, reliable and detailed information on this subject. To ascertain what patents had been issued to the different inventors of the processes of electric smelting, the countries where they had been issued, and full particulars thereof. Photographs and accurate drawings (where necessary) of the

various parts of apparatus and plants employed were to accompany my report.

The following constituted the members of the staff under my direction: Mr. C. E. Brown, E. E.; Mr. F. W. Harbord, metallurgist; Mr. Erik Nystrom, M. E.; draftsman; Mr. Thomas Cote, secretary.

The results of the investigation of the Commission have been laid down in a report entitled "Report of the Commission Appointed to Investigate the Different Electrothermic Processes for the Smelting of Iron Ores and the Making of Steel in Operation in Europe." This report has been widely distributed, copies having been sent on requisition to Russia, Germany, Italy, France, Sweden, England, Brazil, Honolulu, New Zealand, Japan, India, Canada and the United States, showing the interest taken in and desire for information on the subject of electric smelting.

The only experiments which the members of the Commission were able to witness in the electric smelting of iron ores were those made by Dr. Hérault, at La Praz, and Mr. Keller, of Keller, Leleux & Co., at Livet, France. The first was a mere trial, furnishing no reliable quantitative results; the latter, more extended experiments, continued for a number of days, were made with a very porous hematite containing 3.21 per cent. of manganese and only 0.02 per cent. of sulphur, an ore, therefore, easily reduced and easily desulphurized. Two sets of experiments were made at Livet. In the first experiment 0.475 horse-power years were required per ton of 2,000 pounds of pig iron, corresponding to an output of 5.769 tons per 1,000 horse-power days. In the second experiment 0.226 horse-power years were required per ton of product, corresponding to an output of 12.12 tons per 1,000 horse-power days. In this experiment, moreover, most of the iron produced was white, for which cold working is required and consequently less energy consumed.

The difference in output of these two experiments was so great, being more than double that of the first in the second experiment, that no conclusion could be drawn as to the amount of energy required per ton of product and Mr. Harbord, the metallurgist of the Commission, was compelled to adopt 0.350 horse-power years, the mean of the two experiments, as the probable energy required per ton of product. This would correspond to an output of 7.827 tons per 1,000 electric horse-power days.

Before, therefore, a sound judgment could be formed as to the practicability of the electrothermic process for the smelting of Canadian ores it was desirable to establish with some degree of exactitude the amount of electric energy required per ton of product and also the following important points referring to Canadian conditions, which were either not taken up or were left in doubt by the Livet experiments:

*First*—Can magnetite, which is our chief ore and which is to some extent a conductor of electricity, be successfully and economically smelted by the electric process?

*Second*—Can iron ores with comparatively high sulphur content but not containing manganese be made into pig iron of marketable composition?

*Third*—The experiments made at Livet with charcoal as a reducing agent in substitution for coke having failed, could the process be so modified that charcoal, which can be cheaply made from mill refuse and other sources of wood supply useless for other purposes, could be substituted for coke? This is especially important since charcoal and peat-coke constitute home products, while coal-coke for metallurgical processes requires to be imported into the provinces of Ontario and Quebec.

The settlement of these questions was of such paramount importance for the formation of a judgment as to the feasibility of introducing electric smelting of iron ores as an economic process in those provinces of Canada which lack coal for metallurgical coke, but are abundantly supplied with water-powers and iron ore deposits, that the experimental investigation of the subject by the erection of an electric smelting plant at Sault Ste. Marie, Ont., was authorized.

*Description of Experimental Furnace and Electrode Holder.*—The furnace, as first designed by Dr. Héroult, consisted of an iron casing  $\frac{1}{4}$  inch thick, bolted to a cast-iron plate 48 inches in diameter. This casing was vertically slit to break the magnetic circuit and render the inductance as small as possible. The gap formed by this slit was bridged over by a plate of copper 10 inches wide, which was securely riveted to the iron casing (Figs. 1 and 2).

The bottom plate, which formed one of the terminals for the current, had iron rods cast in, for the purpose of insuring a good contact with the carbon paste rammed into the lower part of the casing which formed the crucible.

# EXPERIMENTAL ELECTRIC FURNACE FOR RUNS 15-19

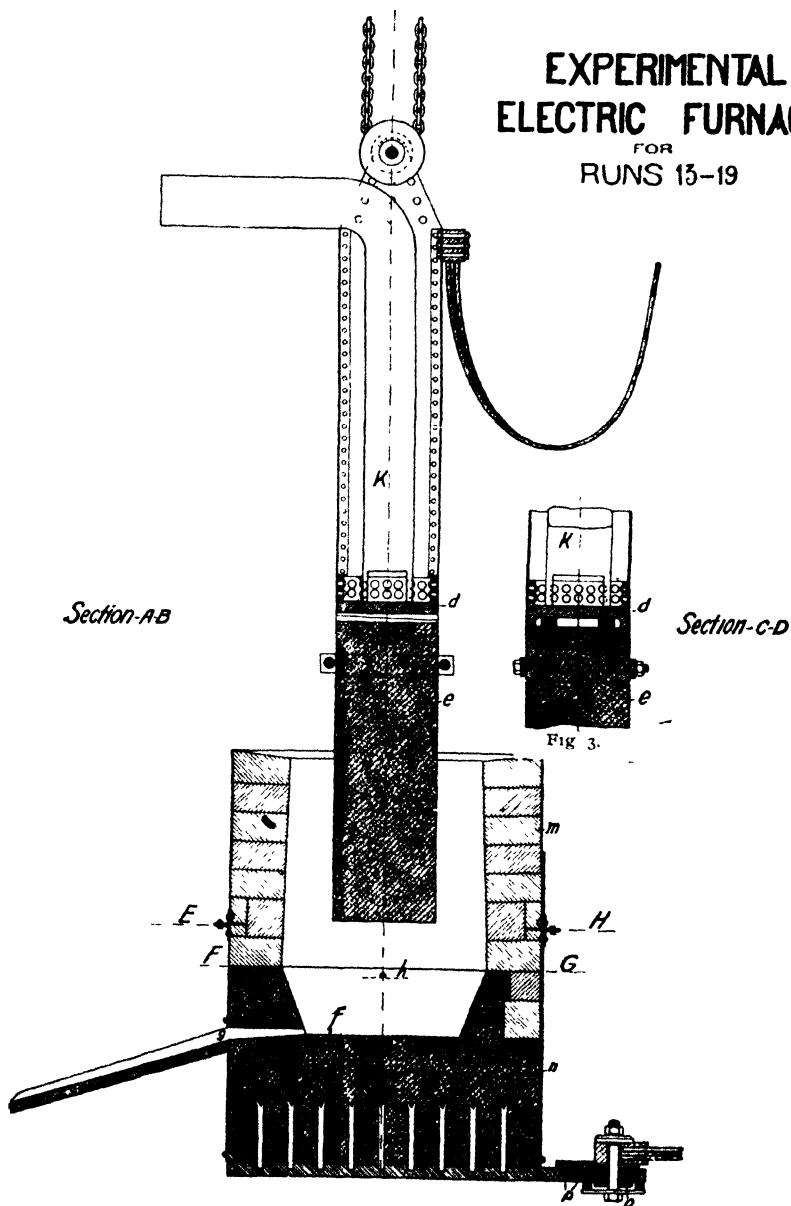


Fig. 1.

The casing was made in two parts, the lower part being 3 feet and the upper 4 feet high.

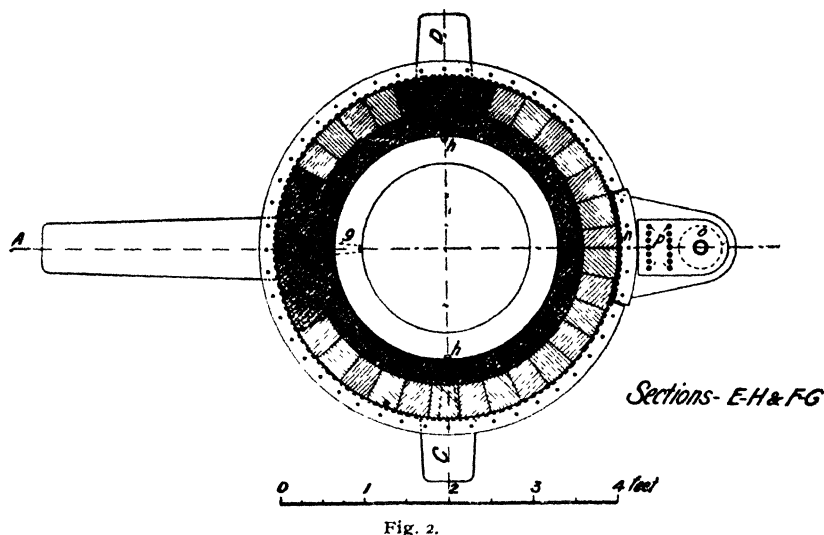


Fig. 2.

The electrode holder was made of four copper plates riveted together and to a steel shoe (*d*), Figs. 1 and 3, into which fitted the electrode (*e*). In this construction the sides of the electrode and electrode holder were flush, which allowed the holder to penetrate the charge without resistance. This was intended to permit of the consumption of the electrode to nearly its full length and obviate the necessity of throwing away from 2 to 3 feet of unused electrode, which in any other construction would be the case. To keep the contact cool a pipe (*k*) was introduced, by means of which air circulation was effected. It was found, however, that to secure proper contact between the steel shoe and electrode a clamp had to be placed around the shoe, Fig. 3, the bolts of which in descending into the charge would have offered resistance to vertical regulation of the electrode. This change in the contact rendered the long copper attachment useless.

To utilize as much of the electrode as possible, the height of the furnace was diminished to dimensions shown in Fig. 1, which represents the final modification of the furnace as used for the majority of the experiments made.

The contact did not prove entirely satisfactory, as there was a constant loss of from 2 to 3 volts, but as this loss could not be

remedied during the experiments a bolt was screwed into the electrode and connected to a voltmeter, which allowed of the determination of loss of volts by taking the difference between the volts indicated in main circuit and on the electrode.<sup>1</sup>

The contact with the bottom plate was at first made by driving a conical copper plug into a conical hole in the projecting part of the bottom plate and making contact by pressing the aluminium block (holding cables), copper plug and bottom plate together by means of a bolt (Figs. 1 and 2). Owing to the oxidation of the surfaces in contact, this method of making contact proved inefficient. A new contact was, therefore, made by turning a copper plug from a block of copper 10 by 12 inches, leaving an oblong flange (Figs. 1 and 2), which was dressed on both sides to make a good bearing. Two rows of holes (*p*), Fig. 2 (14 in all), of  $\frac{3}{4}$  inch diameter were drilled through the copper flange and into the bottom plate for a depth of about 1 inch, into which was run melted aluminium. This aluminium also filled any crevices which existed between the surfaces of contact.

This contact proved to be fairly satisfactory, although a loss of 1 volt or less was realized.

The lining of the furnace was given the shape of a double cone set base to base. Changes in the dimensions of the interior were made from time to time, as indicated by experience, but during the latter part of the experiments they were as follows:

	Inches.
Diameter of bottom of crucible.....	24
Height of lower cone.....	11
Height of upper cone.....	33
Diameter of joint base of the two cones.....	32
Diameter at top of furnace.....	30

The electrodes, manufactured by the Héroult process and imported from Sweden, were prisms of square cross-section, 16 by 16 inches by 6 feet long. The contact with the cables carrying the electric current consisted of a steel shoe riveted to four copper plates which ended in a support for a pulley. The electrode with its contact was supported by a chain passing under the pulley, one end of the chain being fastened to the wall, the other end passing over a winch operated by a worm and worm-

<sup>1</sup> Later an entirely new contact was made, which proved entirely satisfactory.

wheel. This formed a convenient arrangement for regulating the electrode by hand.

*Electrical Machinery.*—The electrical energy was furnished by one phase of a 3-phase, 400 kilowatt, 30 cycle, 2,400 volt, alternating current generator coupled by belt to a 300 horse-power, 500 volt, direct current motor. A current of 2,200 volts was delivered to an oil-cooled transformer of 225 kilowatt capacity, designed to furnish current to the furnace at 50 volts. The transformer was placed in a separate room in the furnace building, close to the furnace. From the transformer the current was led to the bottom plate contact of the furnace and to the electrode contact by conductors consisting each of 30 aluminium cables,  $\frac{5}{8}$  inch in diameter.

The measuring instruments consisted of a voltmeter, an ammeter, a power-factor meter and a recording wattmeter. The transformer and electric meters were manufactured by the Westinghouse Electric and Manufacturing Company.

An additional voltmeter reading from 10 to 80 volts, supplied by the Keystone Electric Company, which proved very satisfactory, was also placed in circuit to serve as a check.

*Experiments.*—A number of experiments required to be made to adjust the capacity of the crucible of the furnace to the energy available and to determine the shape to be given to the interior of the furnace to insure easy passage of the charge into the reducing and melting zones. After this, attempts were made to utilize the calorific energy of the carbon monoxide resulting from the reduction of the ore, which in all experiments so far recorded had been wasted. To accomplish this, air under pressure was introduced into the furnace about 12 inches below the upper level of the charge. The carbon of the charge, in the form of coke dust, was mixed with fire-clay and briquetted to prevent it from being consumed by the air blast. It was hoped that by thus utilizing the carbon monoxide in preheating the charge and partially reducing the ore the output would be materially increased.

It was found, however, that the great heat evolved by the combustion of the carbon monoxide caused the charge to become sticky and to hang. Nor could this be remedied by stoking, the space between the walls of the furnace and the electrode being too narrow. Moreover, the electrode, although it had been protected with asbestos and iron sheeting, was found after the

experiment to have been badly corroded. The furnace was not at all adapted for these experiments and further attempts in this direction were abandoned. The experiments, however, showed that with a differently constructed furnace, in which the electrode is isolated from the charge, the output might be greatly increased by the introduction of an air blast.

The official experiments were begun about the middle of January, the furnace being in operation night and day, with some few intermissions, until the 5th of March. During that time about 150 casts were made, yielding about 55 tons of pig iron.

The following classes of ore were treated:

- (1) Hematite (Negaunee).
- (2) Magnetite from the Wilbur mine, Ont. (Wm. Caldwell, Esq.).
- (3) Magnetite from the Blairton mine, Ont. (Pierce Co., Marimora).
- (4) Magnetite from the Calabogie Mining Co. (J. G. Campbell, Esq., Perth).
- (5) Magnetite from the Calabogie Mining Co. (J. G. Campbell, Esq., Perth).
- (6) Magnetite from the Calabogie mine (T. B. Caldwell, Esq., Lanark).
- (7) Roasted pyrrhotite from Lake Superior Corporation.
- (8) Titaniferous iron ore from Quebec (J. G. Scott, Quebec).

The materials for the charge—ore, flux and carbon—were crushed to pass through a  $\frac{3}{4}$  inch ring and roughly mixed. The composition of the charge in each run as given in this paper was slightly modified from time to time by varying the percentage of charcoal and flux.

*Charging.*—In starting the furnace a small quantity of charcoal was placed on the bottom of the crucible and the electrode lowered until an arc was developed between the charcoal and the electrode. The arc was maintained for from sixteen to twenty hours to pre-heat the furnace. The furnace was then filled up with the charge and by lowering or raising the electrode the current was kept as constant as possible, at 5,000 amperes.

In most experiments when charcoal was used as the reducing agent the electrode occupied a position of about 16 inches from the bottom of the crucible and required very little attention.



RUN NO. 8.<sup>1</sup>

Ore treated.....Hematite  
 Reducing agent.....Briquettes  
 Flux.....Limestone

## ANALYSIS OF RAW MATERIAL.

<i>Hematite.</i>		<i>Limestone.</i>	
SiO <sub>2</sub> .....	5 42	SiO <sub>2</sub> .....	1 71
Fe <sub>2</sub> O <sub>3</sub> .....	88.90	Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> . . . . .	0.81
Al <sub>2</sub> O <sub>3</sub> .....	2.51	CaCO <sub>3</sub> .....	92 85
CaO.....	0 61	MgCO <sub>3</sub> .....	4.40
MgO .....	0 30	P.....	0.004
Mn.....	0 16	S.....	0.052
P.....	0 044		<hr/>
S.....	0.002		99 826
Loss on ignition.....	2 48		
	<hr/>		
	100 426		

Per cent

Metallic iron..... 62.23

The briquettes were made of 80 per cent. coke dust and 20 per cent. fire-clay.

*Briquettes:*

	Per cent.
Volatile matter .....	4 05
Fixed carbon .....	69 73
SiO <sub>2</sub> .....	15 26
Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> .....	8 92
CaO.....	0 90
MgO.....	0 30
S.....	0 84
	<hr/>
	100 00

The charge, which was slightly modified for subsequent charges by increasing the amount of briquettes and decreasing the limestone, had the following composition:

	Pounds
Ore.....	200
Briquettes.....	60
Limestone.....	50

<sup>1</sup> Only those runs are given which are of special interest.

ANALYSIS OF IRON PRODUCED.<sup>1</sup>

<i>Cast No. 28, Grey iron.</i>	<i>Cast No. 30, Grey iron.</i>
Total carbon..... 4.85	..... 4.35
Si..... 0.87	..... 1.03
S..... 0.018	..... 0.019

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	34.40
Al <sub>2</sub> O <sub>3</sub> .....	15.73
CaO. ....	43.53
MgO . ....	2.00
Fe. ....	1.35
S... ..	0.55

$$\frac{\text{Slag (obtained)}}{\text{Iron (obtained)}} = \frac{1162}{2665} = 0.44$$

Length of run. ....	12 hours
Mean volts on furnace .....	38.5
Mean amperes .. . . .	4856
Power factor . . . . .	0.919
Pig iron produced ... ..	2665 pounds
Watts=38.5 × 4856 × 0.919 . . . . .	171812

$$\text{Electrical horse-power} = \frac{171812}{746} = 230.3$$

$$\begin{aligned} \text{Output of pig iron per 1,000 El. horse-power} \\ \text{days} = \frac{2665 \times 24 \times 1000}{12 \times 230.3 \times 2000} \dots\dots\dots 11.57 \text{ tons} \end{aligned}$$

$$\begin{aligned} \text{Electric horse-power years of 365 days per ton} \\ \text{of pig} \dots\dots\dots 0.236 \end{aligned}$$

Subsequent experiments indicate that had charcoal or coke been used as a reducing agent instead of briquettes, thereby greatly reducing the amount of slag produced, the output would have been considerably increased.

## RUN NO. 13.

Ore treated.. . . .	Magnetite from Wilbur mine
Reducing agent .....	Charcoal
Flux.....	Sand

<sup>1</sup> A redetermination for the final report of the composition of slags and iron produced renders the analyses here given subject to amendment.

<i>Wilbur Ore.</i>	Per cent.		<i>Charcoal.</i>	Per cent.
SiO <sub>2</sub> .....	6 20		Moisture .....	14 06
Fe <sub>2</sub> O <sub>3</sub> .....	55.42	} Fe=56.69	Volatile matter.....	28 08
FeO.....	23 04		Fixed carbon . . .	55.90
Al <sub>2</sub> O <sub>3</sub> .....	2 56		Ash .. .. .	2 54
CaO.....	2 00			
MgO... . .	6 84			100 58
P <sub>2</sub> O <sub>5</sub> .....	0 023	P=0 01	Sulphur.....	0 058
S.....	0 01			
CO <sub>2</sub> and undet.....	3 907			
	<hr/>			
	100 000			

The sand used was common furnace sand, of which no analysis was made.

## COMPOSITION OF CHARGE.

	Pounds.
Ore . . . . .	400
Charcoal . . . . .	125
Sand . . . . .	27

## ANALYSIS OF IRON PRODUCED.

<i>Cast No. 49, Grey Iron.</i>		<i>Cast No. 53, Grey Iron</i>	
Total carbon. . .	5.18		4 65
Si. . . . .	1 30		1 41
S . . . . .	0 020		0 012
P. . . . .	0 029		0 024

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	35 84
Al <sub>2</sub> O <sub>3</sub> .....	31 80
CaO .....	14 39
MgO . . . . .	16 22
S .....	0 26
Fe. . . . .	0 35

$$\frac{\text{Slag}}{\text{Iron}} = \frac{4195}{12858} = 0.326$$

Length of run . . . . .	61 hours, 25 min.
Mean volts on furnace .....	35.75
Mean amperes.....	5000
Power factor.....	0 919
Pig iron produced.....	12858 pounds
Watts=35.75 × 5000 × 0 919.....	164271
Electrical horse-power = $\frac{164271}{746}$ .....	220.2

Output of pig iron per 1,000 El. horse-power

$$\text{days} = \frac{12858 \times 24 \times 1000}{61.4 \times 220.2 \times 2000} \dots\dots\dots 11.41 \text{ tons}$$

El. horse-power years<sup>1</sup> per ton of pig. .... 0.2399

RUN No. 14.

Ore treated. .... Magnetite from Blairton mine.

Reducing agent. .... Charcoal

Flux .....  $\left\{ \begin{array}{l} \text{Limestone} \\ \text{Sand} \end{array} \right.$ 

## ANALYSIS OF RAW MATERIAL.

*Blairton Ore.*

SiO <sub>2</sub> .. . . .	6 60	
Fe <sub>2</sub> O <sub>3</sub> .. . . .	60 74	} Fe = 55 85
FeO .. . . .	17 18	
Al <sub>2</sub> O <sub>3</sub> .. . . .	1 48	
CaO .. . . .	2 84	
MgO .. . . .	5 50	
P <sub>2</sub> O <sub>5</sub> .....	0 037	P = 0 016
S .. . . .	0 57	
CO <sub>2</sub> and undet. ....	5 053	

100 000

Charcoal and limestone same as in previous run.

## COMPOSITION OF CHARGE.

	Pounds.
Ore. ....	400
Charcoal .....	125
Limestone.....	25
Sand .....	6

## ANALYSIS OF IRON PRODUCED.

*Cast No 80, Grey Iron.*

Total carbon. . . . .	3 73
Si. ....	3.53
S.....	0 042
P.....	0 034

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	33.80
Al <sub>2</sub> O <sub>3</sub> .....	10.20
CaO .....	21.78
MgO .....	30.50
S .....	2 05
Fe . ....	0 25

$$\text{Slag} = \frac{4892}{11989} = 0.41$$

Length of run. .... 65 hours, 30 min.

Mean volts on furnace. .... 36 03

Mean amperes. .... 4987

Power factor. .... 0 919

<sup>1</sup> 365 days.

Pig iron produced.....	11989 pounds
Watts= $36.03 \times 4987 \times 0.919$ .....	165125
Electrical horse-power= $\frac{165125}{746}$ .....	221.34
Output of pig iron per 1000 El. horse-power	
days= $\frac{11989 \times 24 \times 1000}{65.5 \times 221.34 \times 2000}$ .....	9.92 tons
El. horse-power year per ton of pig.....	0.276

## RUN NO. 15.

Ore treated .....	Magnetite from Calabogie <sup>1</sup>
Reducing agent.....	Charcoal and charcoal braise
Flux .....	Limestone

## ANALYSIS OF RAW MATERIAL.

*Calabogie Ore.*

SiO <sub>2</sub> .....	3 80	} Fe=59 38
Fe <sub>2</sub> O <sub>3</sub> .....	56.24	
FeO.....	25 76	
Al <sub>2</sub> O <sub>3</sub> .....	3 73	
CaO.....	2 00	
MgO.....	3 42	
P <sub>2</sub> O <sub>5</sub> .....	0 85	P=0.371
S. ....	0 20	
CO <sub>2</sub> and undet.....	4 00	
<hr/>		
100 00		

Limestone and charcoal the same as in previous runs. The charcoal braise used was of poor quality, being wet, high in ash and mostly fines.

The composition of the charge, when using charcoal, was:

	Pounds.
Ore....	400
Charcoal.....	125
Limestone ...	30

When using charcoal braise, the composition of the charge was:

	Pounds.
Ore....	400
Charcoal braise.....	145
Limestone.....	40

During this run the alternator had to be stopped on account of repair of motor. The furnace was then considerably cooled and some time was consumed before it was again in working condition.

<sup>1</sup> Calabogie Mining Company.

## FIRST PART OF RUN—ANALYSIS OF IRON PRODUCED.

<i>Cast No. 89, Grey iron.</i>	<i>Cast No. 90, Grey iron.</i>
Total carbon..... 3.53	..... 3.43
Si..... 0.95	..... 1.17
S..... 0.024	..... 0.016
P..... 0.554	..... 0.457

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	24.30
Al <sub>2</sub> O <sub>3</sub> .....	27.16
CaO.....	36.06
MgO.....	10.74
S.....	1.67
Fe.....	0.25

$$\frac{\text{Slag}}{\text{Iron}} = \frac{1335}{4520} = 0.29$$

Length of run . . . . . 23 hours, 50 min.

Mean volts on furnace..... 36.16

Mean amperes. .... 5.000

Power factor..... 0.919

Pig iron produced . . . . . 4520 pounds

Watts=36.16 × 5000 × 0.919..... 166155

Electrical horse-power =  $\frac{166155}{746}$  . . . . . 222.72

Output of pig iron per 1000 El. horse-power

$$\text{days} = \frac{4520 \times 24 \times 1000}{23.83 \times 222.72 \times 2000} \dots\dots\dots 10.21 \text{ tons}$$

El. horse-power year per ton of pig..... 0.268

## SECOND PART OF RUN—ANALYSIS OF IRON PRODUCED.

<i>Cast No. 92, Grey iron.</i>	<i>Cast No. 95, Grey Iron.</i>
Si.....     ° 73	° 95
S.....     0.011	0.012

$$\frac{\text{Slag}}{\text{Iron}} = \frac{892}{2722} = 0.33$$

Length of run . . . . . 16 hours, 15 min.

Mean volts on furnace..... 35.85

Mean amperes..... 5000

Power factor..... 0.919

Pig iron produced..... 2722 pounds.

Watts=35.85 × 5000 × 0.919..... 164730

Electrical horse-power =  $\frac{164730}{746}$  ..... 220.81

Output of pig iron per 1000 El. horse-power

$$\text{days} = \frac{2722 \times 24 \times 1000}{16.25 \times 220.81 \times 2000} \dots\dots\dots 9.10 \text{ tons}$$

El. horse-power year per ton of pig..... 0.301

## RUN No. 16.

Ore treated..... Magnetite from Calabogie<sup>1</sup>  
 Reducing agent..... Charcoal  
 Flux. .... { Limestone  
                   Quartz

## ANALYSIS OF RAW MATERIAL.

*Calabogie Ore.*

SiO <sub>2</sub> .....	6.06	} Fe=59 85
Fe <sub>2</sub> O <sub>3</sub> .....	58 00	
FeO.....	24 78	
Al <sub>2</sub> O <sub>3</sub> .....	1 00	
CaO. ....	0 40	
MgO. ....	6 00	
P <sub>2</sub> O <sub>5</sub> .....	0 046	P=0.020
S... ..	0.17	
CO <sub>2</sub> and undet.....	3 544	

---

 100 000
*Charcoal.*

Moisture ...	2 20
Volatile matter ...	20 60
Fixed carbon ...	74 40
Ash. ...	2 80

Limestone same as in previous runs.

## COMPOSITION OF CHARGE.

	Pounds.
Ore . . . . .	400
Charcoal . . . . .	125
Limestone.....	45
Quartz . . . . .	5

## ANALYSIS OF IRON PRODUCED.

*Cast No. 102, Grey Iron.*

Total carbon ..	4 20
Si.. ..	1 75
S . . . . .	0 005
P . . . . .	0 047

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> . ....	30.90
Al <sub>2</sub> O <sub>3</sub> .....	12.30
CaO . . . . .	40.09
MgO... ..	12.91
S . . . . .	1.48
Fe... ..	0.56

$$\frac{\text{Slag}}{\text{Iron}} = \frac{2556}{7150} = 0.36$$

<sup>1</sup> Calabogie Mining Co., Shaft No. 4.

Length of run.....	38 hours, 20 min.
Mean volts on furnace.....	36.5
Mean amperes.....	4993
Power factor.....	0.919
Pig iron produced.....	7150 pounds.
Watts= $36.5 \times 4993 \times 0.919$ .....	167483
Electrical horse-power = $\frac{167483}{746}$ .....	224.50
Output of pig iron per 1000 El. horse-power	
days = $\frac{7150 \times 24 \times 1000}{38.33 \times 224.50 \times 2000}$ .....	9.97 tons

## RUN No. 17.

Ore treated. . . . .	Magnetite from Calabogie mine <sup>1</sup>
Reducing agent.....	Charcoal
Flux . . . . .	{ Limestone Quartz

## ANALYSIS OF RAW MATERIAL.

*Calabogie Ore.*

SiO <sub>2</sub> . . . . .	4 00	
Fe <sub>2</sub> O <sub>3</sub> .....	55 31	} Fe=58 29
FeO.....	25 20	
Al <sub>2</sub> O <sub>3</sub> .....	2.24	
CaO.....	2 40	
MgO.....	4 00	
P <sub>2</sub> O <sub>5</sub> .....	0 95	P=0.415
S. ....	0 45	
CO <sub>2</sub> and undet.....	5 45	
	<hr/>	
	100 00	

Charcoal same as in run No. 15. Limestone same as in previous runs.

## COMPOSITION OF CHARGE.

	Pounds.
Ore.....	400
Charcoal.....	125
Limestone .....	20

Occasionally small quantities of quartz were added.

## ANALYSIS OF IRON PRODUCED.

<i>Cast No. 111, Grey Iron.</i>	<i>Cast No. 113, Grey Iron.</i>
Si..... 1.49	1.55
S..... 0.016	0.015
P..... 0.500	0.520

<sup>1</sup> T. B. Caldwell, Esq.



## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	26.96
Al <sub>2</sub> O <sub>3</sub> .....	20.64
CaO.....	27.40
MgO.....	15.50
S.....	1.41
Fe.....	0.21

$$\frac{\text{Slag}}{\text{Iron}} = \frac{3263}{8303} = 0.39$$

Length of run.....	43 hours, 5 min
Mean volts on furnace.....	36.79
Mean amperes.....	5000
Power factor.....	0.919
Pig iron produced.....	8303 pounds.
Watts=36.79 × 5000 × 0.919.....	169050
Electrical horse-power = $\frac{169050}{746}$ .....	226 6
Output of pig iron per 1,000 El. horse-power	
days = $\frac{8303 \times 24 \times 1000}{43.08 \times 226.6 \times 2000}$ .....	10.20 tons
El. horse-power year per ton of pig.....	0.268

## RUN NO. 18.

Ore treated.....	Roasted pyrrhotite
Reducing agent.....	Charcoal
Flux.....	Limestone

## ANALYSIS OF RAW MATERIAL.

*Roasted Pyrrhotite.*

SiO <sub>2</sub> .....	10.96
Al <sub>2</sub> O <sub>3</sub> .....	3 31
Fe <sub>2</sub> O <sub>3</sub> .....	65.43
CaO.....	3.92
MgO.....	3 53
S.....	1.56
P.....	0 016
Cu... ..	0 41
Ni.....	2.23
Metallic iron.....	45.80

Charcoal and limestone same as in previous run. The limestone in the charge was decreased from 120 pounds when starting to 50 pounds. The composition then being:

## Pounds.

Ore.....	400
Charcoal.....	110
• Limestone.....	50

## ANALYSIS OF IRON PRODUCED.

<i>Cast No. 125.</i>	<i>Cast No. 130.</i>	<i>Cast No. 133.</i>
Total carbon... 3.23	3.38	2.50
Si..... 4.90 <sup>1</sup>	4.50 <sup>1</sup>	6.32 <sup>1</sup>
S..... 0.007	0.006	0.007
P..... 0.062	0.037	0.042
Cu... 0.86	0.87	0.71
Ni. . . . . 3.70	4.12	4.00

## ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	16.44
Al <sub>2</sub> O <sub>3</sub> .....	13.86
CaO.....	53.25
MgO.. . . .	8.80
S.....	5.28
Fe... . . . .	0.65
Cu.....	trace
Ni.....	trace

$$\frac{\text{Slag}}{\text{Iron}} = \frac{5060}{7336} = 0.69$$

Length of run..... 56 hours, 20 min.

Mean volts on furnace..... 36.05

Mean amperes..... 5000

Power factor..... 0.919

Pig iron produced (ferro-nickel). . . . . 7336 pounds.

Watts=36.05 × 5000 × 0.919 . . . . . 165649

Electrical horse-power =  $\frac{165649}{746}$  . . . . . 222.05

Output of pig iron (ferro-nickel) per 1000 El.

$$\text{horse-power days} = \frac{7336 \times 24 \times 1000}{56.33 \times 222.05 \times 2000} = 7.038 \text{ tons}$$

El. horse-power year per ton of pig. . . . . 0.389

## RUN NO. 19.

Ore treated..... Titaniferous iron ore

Reducing agent..... Charcoal

Flux.....  $\left\{ \begin{array}{l} \text{Limestone} \\ \text{Fluorspar} \end{array} \right.$

## ANALYSIS OF RAW MATERIAL.

*Titaniferous Iron Ore.*

SiO <sub>2</sub> .....	7.12	$\left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Fe} = 43.59$
Fe <sub>2</sub> O <sub>3</sub> .....	30.30	
FeO .....	28.78	
Al <sub>2</sub> O <sub>3</sub> .....	7.00	

<sup>1</sup> By increasing the limestone of the charge the silicon content of the ferro-nickel pig recently produced has been depressed to 2 per cent.

CaO.....	1.00	
MgO.....	4.14	
P <sub>2</sub> O <sub>5</sub> .....	0.064	P=0.028
S.....	0.04	
TiO <sub>2</sub> .....	17.82	
Cr <sub>2</sub> O <sub>3</sub> .....	2.50	Cr=1 42
<hr/>		
99.684		

Charcoal and limestone same as in previous run.

#### COMPOSITION OF CHARGE.

	Pounds.
Ore.....	400
Charcoal.....	100
Limestone.....	50
Fluorspar.....	50

#### ANALYSIS OF PIG IRON PRODUCED.

<i>Cast No. 136.</i>	<i>Cast No. 137.</i>
Total carbon.....	3 50
Si.....	4.50
S.....	0 007
P.....	0.143
Ti (approx.).....	1 00
	1.30

#### ANALYSIS OF SLAG PRODUCED.

SiO <sub>2</sub> .....	7 00
Al <sub>2</sub> O <sub>3</sub> .....	28 50
CaO.....	14.23
MgO.....	2 93
TiO <sub>2</sub> .....	38 92
Fe.....	1.13
S.....	0 90

On account of the furnace being in a very bad condition, the lining being eaten away by the limy slag used in the previous run, the run had to be stopped and no figures as to output could be obtained.

The slag was very fluid and likely the fluorspar in the charge could have been reduced considerably or omitted altogether.

The iron obtained in cast No. 136 was probably mixed with some iron from the previous charge, when ore with high phosphorus content was used.

*The Smelting of Magnetite.*—It was expected that considerable difficulty would be experienced in the smelting of magnetite, on account of its conductivity. It was thought that with the furnace

in use, in which the electrode was immersed in the charge, the current would disseminate itself laterally from the sides of the electrode through the charge, preventing the current at the reducing and fusion zone from attaining such density as would be required for the high temperature necessary for reduction and fusion. With charcoal as a reducing agent this difficulty was not experienced, nor was the inductance of the furnace increased by the presence of magnetite.

It should, however, be mentioned that the phenomenon of rapid temporary decrease of ohmic resistance of the charge shortly after the current is put on, when the charge consists of conductors in the form of small pieces, described by J. Bronn, in his article entitled "Zur Anwendung lose geschichteter kleinstückiger Leiter für elektrische Heizwiderstände,"<sup>1</sup> was occasionally observed in some of the runs made. This trouble occurred chiefly at the beginning of a new experiment, before the furnace had acquired its normal temperature. By adding a few shovels of iron ore, omitting flux and charcoal, it was sometimes possible to cause the electrode, which to keep the current constant had by hand regulation been elevated, to return to its normal position. In a few instances, however, this method failed, especially when the furnace was choked with fines and the gases evolved escaped under great pressure. Since the electric installation did not permit the compensation of the temporary increase of conductivity of the charge by decrease of voltage with constancy of current, the electrode in such case rose to the top of the furnace and it became necessary to melt down the charge and start anew.

If the explanation offered by Bronn is correct that the decrease of the ohmic resistance during the "Anheizungsphase" is occasioned by the more intimate contact of the conducting pieces of the charge due to pressure of escaping gases from the pores of the carbon and the carbon dioxide evolved from the limestone, it is evident that preheating the charge, which might be effected by utilizing the carbon monoxide resulting from reduction, would entirely overcome this difficulty, if the charge were sufficiently porous to permit the gases evolved to escape at low pressure. Under such conditions the electrode would maintain its normal position throughout the operation, requiring to be lowered only to keep step with its consumption.

<sup>1</sup> "Electrotechnische Zeitschrift," 1906, Heft 9.

The ores treated, with the exception of the hematite and the roasted pyrrhotite, contained a high percentage of magnesia, producing a very infusible slag. When the furnace had been running for some time this infusible material formed a scale around the crucible, the electric energy available not being sufficient to keep it in a molten condition. The crucible and lower part of the furnace were, therefore, partially filled up, preventing easy access of the charge to the reducing and melting zone. This slower feeding left the charcoal on top of the furnace exposed to the air a longer time, thus increasing the amount of charcoal required and decreasing the output. With a greater current than was available and consequent higher temperature, the formation of the scale would have been prevented and the output correspondingly increased.

The electric installation at our disposal was far from ideal for electric smelting experiments. Aside from the drop of voltage due to the frequent slipping of the belt connecting motor and generator, it was impossible to increase the current beyond 5,000 amperes at from 35 to 40 volts. This inelasticity of the system prevented the determination of the most suitable current and voltage for a given charge in the furnace.

*The Use of Charcoal as a Reducing Agent.*—It was of great importance to ascertain whether charcoal without being briquetted with the ore could be used instead of coal-coke. No difficulty whatever was experienced, in fact so admirably adapted was charcoal, when crushed to pass a  $\frac{3}{4}$  inch ring, as a reducing agent in the electric furnace that coke and briquettes of coke with clay were abandoned and all the experiments with magnetite and roasted pyrrhotite described were made with charcoal. Some of the charcoal available was of very poor quality, being little better than charred wood containing only about 56 per cent. of fixed carbon. This and the fact that a considerable quantity of the charcoal was consumed on top of the furnace account for the large quantity of charcoal used per ton of product. A modification of the furnace, protecting the upper layer of the charge from the atmosphere, and the use of charcoal properly carbonized would decrease considerably the amount of charcoal which was actually used in the experiments and consequently reduce the cost of production as given.

*Consumption of Electrode.*—For the production of 42,711 pounds

of pig iron, 384 pounds of electrode were consumed, the same electrode having been in commission for thirteen days.

Consumption of electrode per ton of pig iron:

$$\frac{384 \times 2000}{42711} = 17.98 \text{ pounds.}$$

During the time this electrode was in commission the material in the furnace was melted down several times, exposing the red hot electrode to the oxidizing atmosphere. The consumption of electrode was found to be greater for white iron than for grey iron and since the 42,711 pounds of pig iron produced included several casts of white iron, the consumption of electrode was also on that account greater than it would have been had only grey iron been produced.

*Power Factor.*—The power factor of the furnace was determined by Mr. Chas. Darrall, of the Canadian Westinghouse Company of Hamilton, Ont., and was found to be 0.919. This high power factor is due to the construction of the furnace casing, as described above.

Since the true electric power is the apparent electric power multiplied by the power factor, it is evident that any error made in the determination of the power factor which tends to decrease its value will appear to decrease the consumption of energy per ton of product. The large output of 12.12 tons per 1,000 electric horse-power days, *i. e.*, the small amount of electric horse-power absorbed per ton of product in the second Livet experiments, was obtained in a furnace with the abnormally low power factor 0.564. Whatever doubt may be engendered as to the correctness of the figure obtained for the absorption of electric energy on account of this low power factor of the Keller furnace, such doubt cannot arise regarding the figures obtained with the Héroult furnace for the absorption of electric energy in the Government experiments on account of its remarkably high power factor 0.919.

Moreover, since the cost of alternate current generators increases with increase of capacity, furnaces with high power factors (which can utilize a high percentage of the capacity of the generators) will be more economical as regards the first cost of the electrical installation of an electric smelting plant than furnaces with low power factors.

*Modification of Experimental Furnace for Commercial Production of Pig Iron.*—Probably the largest unit which can at present be constructed on the model of the experimental furnace will not exceed 1,500 horse-power. The construction of the experimental furnace to fit it for the production of pig iron on a commercial scale will require to be modified in the following important particulars:

(1) The top of the furnace requires to be modified to permit of the application of labor-saving machinery for charging.

(2) Provision requires to be made for the collection and utilization of the carbon monoxide produced by the reduction of the ore; this involves also the protection of the charcoal of the charge from combustion on top of the furnace.

The greater capacity insuring less loss of heat by radiation and the modification of the furnace to permit of the utilization of the carbon monoxide will materially increase the output beyond that ascertained by the experimental furnace. The experiments indicated that under *normal* conditions about 11.5 tons were produced by an expenditure of 1,000 electric horse-power days (see runs Nos. 8 and 13). It is, therefore, not unreasonable to assume that under similar conditions with a properly constructed plant the output per 1,000 horse-power days would certainly reach 12 tons. This figure has been adopted in calculating cost of production per ton of pig.

The protection of the charcoal of the charge from combustion on top of the furnace will materially decrease the amount of charcoal necessary for reduction and consequently lessen the cost of this item. This saving has, however, not been taken into account in the estimate of cost.

On account of the value of the product, the smelting of roasted nickeliferous pyrrhotite by the electrothermic process, as carried out with the Government experimental plant, admits of immediate commercial application without other modification of the furnace than increase of its capacity.

The Lake Superior Corporation has acquired the Government plant by purchase and employs it for the semi-commercial production of ferro-nickel pig. The company has had the furnace in operation night and day since about March 7th. The smelting operations are left entirely in the hands of the workmen, who had been trained during the progress of the Government ex-

periments. I am informed that the furnace works with admirable regularity, the regulation of the electrode requiring hardly any attention, and the output is of excellent and uniform quality.

*The Electric Furnace as Compared with the Blast-Furnace.*—The tendency among iron manufacturers for some time has been to increase the size and capacity of blast-furnaces until the enormous capacity of 600 to 800 tons per day with a furnace stack 100 feet high has been reached.

But for the economical working of a blast-furnace there is a point beyond which the furnace can be neither increased nor decreased in size. It seems to have been established that furnaces with a height of 90 feet and corresponding output prove the most economical. While fuel is cheap and ore of good quality and high iron content is still abundant, any disadvantages of such large units will not be felt. It may, however, be of value to call attention to some of the disadvantages connected with the employment of large units. These are as follows:

*First*—Large first cost of furnace.

*Second*—Excessive cost of charging machinery and upkeep of same.

*Third*—Large expense and probable idleness through breakdown.

*Fourth*—Cost of and difficulties of making repairs, relining, etc.

*Fifth*—Serious complications resulting from scaffolding, involving loss of life and money.

*Sixth*—Financial loss resulting from wrong composition of charge, involving many tons of iron before correction can be made.

Yet, with even these drawbacks the blast-furnace of to-day, representing the result of a hundred years' experience and inventive skill, must be pronounced a perfect machine, hardly permitting further improvement, and if the electric furnace, which is yet in its infancy, is able in its present state of development to compete with a blast-furnace under the special conditions of cheap electric energy and high price of metallurgical fuel, what may we not expect of its performance when all the calories available in an electric furnace will have been utilized by proper design, as the result of years of experience?

It is, therefore, scarcely to the point to speak of faults or disadvantages of a new invention, which, as they are realized, may be corrected, but it is of great importance to point out any advantages



a new apparatus may possess over a long-tried machine. The following are some points in favor of the electric furnace:

*First*—Original small cost of furnace.

*Second*—Absence of bulky or costly charging machinery.

*Third*—Small expense involved through breakdown.

*Fourth*—Small cost and ease with which repairs may be made.

*Fifth*—No serious complications arising from scaffolding.

*Sixth*—Loss due to wrong composition of charge reduced to a minimum.

*Seventh*—Perfect control of the temperature in the reducing and melting zone.

In reviewing the advantages arising from the introduction of the electric furnace, it must be understood that a smelting plant operated by electricity is composed of several small units, the disablement of any one of which will not render the plant idle.

Again, in case of accident, such a furnace will cool down in a comparatively short time, permitting repairs to be made in the least possible time.

*General Remarks.*—The far-reaching consequence of the gratifying results achieved by these experiments will at once be apparent. Many of our magnetites are too high in sulphur to be handled by the blast-furnace and consequently have so far been of no commercial value. But the very best of pig iron, as has been proven, can be made from ores which contain as high as 1.5 per cent. of sulphur. A blast-furnace will not usually handle an ore which contains more than 0.1 per cent. of sulphur and requires, therefore, an ore which cannot be obtained at a low figure.

Regarding the water-power required for the application of this process it may be stated that many water-powers exist in Ontario and Quebec, surrounded by iron ore fields, in localities ill adapted for the application of electric energy for any other purpose and could be developed to furnish an electric horse-power year for from \$4.50 to \$6.00.

With such a price for the energy required, the small consumption of electrode, the cheapness of the ore employed and the peculiar excellence of the pig iron produced, electric smelting of iron ores in Canada, using charcoal or peat-coke made from our peat bogs of enormous extent, may be pronounced commercially feasible.

Under the prevailing conditions in Canada it now only remains for the engineer to design a plant on a commercial scale, say of 100 to 150 tons daily output, with all the necessary labor-saving appliances. Just as in the case of the blast-furnace so likewise with the electric furnace, experience gained will result in further economy and the day may not be far distant when the carbon monoxide, which is of high calorific value and which at present as a product of the reaction taking place in the electric furnace is allowed to escape without utilization, will be employed for increasing the output by something like one-fourth. When this is accomplished, the blast-furnace could not compete with the electric furnace, even under conditions where coke might be cheaper than at present quoted in Ontario and Quebec.

With the present advance which has been made in the transmission of electric energy, batteries of electric furnaces could be set up at various iron ore deposits, which could be fed with electric energy from some centrally located water-power, thus effecting a saving of the transportation costs of the ore from the mine to the furnace.

The following is a summary of the results of the experiments which have been made under Government auspices at Sault Ste. Marie:

*First*—Canadian ores chiefly magnetite can be economically smelted by the electrothermic process.

*Second*—Ores of high sulphur content can be made into pig iron containing only a few thousandths of a per cent. of sulphur.

*Third*—The silicon content can be varied as required for the class of pig to be produced.

*Fourth*—Charcoal which can be cheaply produced from mill refuse or wood which could not otherwise be utilized and peat-coke made from peat can be substituted for coke without being briquetted with the ore.

*Fifth*—A ferro-nickel pig can be produced practically free from sulphur and of fine quality from roasted nickeliferous pyrrhotite.

*Sixth*—Pyrite cinders, resulting from the roasting of pyrite in the manufacture of sulphuric acid and which at present constitute a waste product, can be smelted into pig iron by the electric process.

*Seventh*—Titaniferous iron ores containing up to 5 per cent. can be successfully treated by the electrothermic process. This conclusion is based upon an experiment made with an ore containing 17.82 per cent. of titanitic acid, yielding a pig iron of good quality.

The results of the introduction of electric smelting into countries possessing iron ore deposits and water-powers but lacking metallurgical fuel may be summarized as follows:

*First*—The utilization of water-powers which cannot at present be profitably employed for any other purpose.

*Second*—The utilization of iron ore deposits, which on account of their high sulphur content cannot be treated by blast-furnace methods and have so far been valueless. This is of extreme importance, for already the question has arisen, how long the present supply of blast-furnace iron ore is likely to last and ores are now accepted by furnace men with a metallic content such as would not have been looked at a few years ago, and when these ores are exhausted and none but sulphurous ores or titaniferous ores are available, the stacks of the numerous blast-furnaces, which have rendered such magnificent service to our present civilization, will be silent and smokeless, having been supplanted by the electric furnace which can successfully treat an ore which the blast-furnace cannot handle.

*Third*—The utilization of peat bogs for the production of peat coke, to be used as reducing material for the operation of electric furnaces, and utilization of mill refuse and sawdust, for which there has so far been no practical use.

*Fourth*—Rendering such countries independent of fuel import for metallurgical processes.

*Fifth*—Enabling them to produce their own pig iron for home consumption and consequently retaining in their country the money which otherwise would have to be sent abroad to purchase pig iron in the crude and manufactured state.

*Sixth*—The development of steel plants and rolling mills using only electric energy.

ESTIMATE FOR A 10,000 HORSE-POWER PLANT<sup>1</sup> PRODUCING 120 TONS OF PIG IRON PER DAY OF TWENTY-FOUR HOURS.

Furnaces, contacts, overhead work.....	\$ 24,500
Bins, chutes, elevators.....	14,000
Crushers.....	4,000
Hoists and regulators.....	10,500
Instruments.....	1,400
Cables for conductors.....	8,400
Building.....	10,500
Mixer and casting machine.....	10,000
Traveling crane and tracks.....	5,000
Ladles.....	1,500
Slag trucks.....	3,000
Ore bins.....	3,000
Repair shop.....	5,000
	<hr/>
	\$100,800
Charcoal plant.....	50,000
Power plant (assuming cost of developing one electric horse-power = \$50.00).....	500,000
	<hr/>
	\$650,800
Electrode plant.....	6,000
Unforeseen expenditure.....	43,200
	<hr/>
	\$700,000
Amortization: 5 per cent } Depreciation: 5 " " } 15 per cent. on \$700,000....	105,000
Interest: 5 " " }	
On a production of 43,200 tons per year of 360 days per ton of pig iron.....	\$ 2.43

COST OF PRODUCTION PER TON PIG IRON.

Ore (55 per cent. metallic iron) at \$1.50 per ton....	\$ 2.70
Charcoal, one-half ton at \$6.00 per ton.....	3 00
Electric energy, amortization, etc.....	2.43
Labor.....	1.00
Limestone.....	0 20
Eighteen lbs. of electrode at 2 cents per lb.....	0.36
General expenses.....	1.00
	<hr/>

Total.....\$ 10.69

The figures here given on the authority of Dr. Héroult are outside figures and I desire to make the following remarks respecting them:

<sup>1</sup> This estimate is given on the authority of Dr. R. Héroult.

*First*—The price of ore will depend upon its quality and on local conditions and is not, therefore, a fixed figure.

*Second*—As stated previously, many water-powers in Ontario and Quebec can be developed to furnish an electric horse-power year at from \$4.00 to \$5.00. This lower cost will reduce the electric energy required per ton of pig, as stated in the estimated cost.

*Third*—A better class of charcoal than was available for the experiments and proper protection against its consumption on top of the furnace will materially decrease the quantity of charcoal required per ton of pig, as stated in the cost sheet, and consequently lower the cost of production below the figures stated.

DEPARTMENT OF MINES,  
OTTAWA, CANADA.

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## FORMALDEHYDE DISINFECTION. DETERMINATION OF THE YIELD OF FORMALDEHYDE IN VARIOUS METHODS OF LIBERATING THE GAS FOR THE DISINFECTION OF ROOMS.<sup>1</sup>

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IN the multitude of experiments on disinfection by formaldehyde gas very few of the experimenters have made any attempt to determine the exact amount of formaldehyde gas that entered the room from the charging apparatus. Several writers make reference to the percentage of the gas present in the air of the room, but they either do not state how the determinations were made or they obtain the percentage indirectly;<sup>2</sup> M. von Brunn,<sup>3</sup>

<sup>1</sup> These experiments were performed in the Division of Pharmacology, Hygienic Laboratory, U. S. Public Health and Marine Hospital Service, and are published by the permission of Surgeon-General Wyman; the results are incorporated in Bulletin 27, of the Hygienic Laboratory, where they are used by Dr. T. B. McClintic to illustrate his bacteriological results.

<sup>2</sup> Kinyoun: "Formaldehyde as a Disinfecting Agent and its Practical Application," Pub. Health Rep., U. S. P. H. & M. H. S., Jan. 29, 1897; Sprague: "Rapid Disinfection with High Percentages of Formaldehyde," Medical News, Dec. 11, 1897 (work done in the Hyg. Lab., U. S. P. H. & M. H. S.); Hill and Rickards: "Notes on Formaldehyde," Proc. 13th Ann. Meeting, Am. Pub. Health Assn., Dec. 9-12, 1902 (work done in Boston Board of Health Bacteriological Laboratory).

<sup>3</sup> v. Brunn: "Formaldehydesinfection durch Verdampfung verdünnten Formalins" (Breslauer Methode), Z. Hygiene und Infektionskrankheiten, 30, 201 (1899).\*

however, made determinations directly on the charged air of a room by drawing 20 liter volumes of the air through water and titrating the formaldehyde absorbed by the iodine method. In those cases where the percentage of formaldehyde in the air of the room has been referred to, it was in connection with the particular method of charging with which the experimenter happened to be working. In my experiments the attempt has been made to determine the amount of formaldehyde gas given off into a room from a definite volume of formalin by five different methods, and from the results, to fix the relative standing of these methods as to the yield of formaldehyde gas.

These experiments were suggested by the publication of a new method of liberating formaldehyde gas from formalin, proposed in 1904 by Henry D. Evans, chemist, and Dr. J. P. Russell, bacteriologist, of the Laboratory of Hygiene, Augusta, Me.<sup>1</sup> The method consists in pouring the formalin quickly upon fine crystals of potassium permanganate, contained in a suitable metallic vessel. It was tested by Russell on over fifteen hundred cultures of bacteria exposed in different parts of rooms of various locations and dimensions. The results indicate this method of liberating the gas to be an efficient one, and if the same results be found by others, this method no doubt will supplant some of the older and more cumbersome methods, because of its ideal simplicity, the rapidity with which a room can be charged, and the inexpensive apparatus required. The Evans-Russell method seems an anomalous one as the formaldehyde gas is obtained by a process which destroys a part of the substance, and it was thought to be desirable to determine how much of the gas is given off in a room from a definite volume of formalin. For the sake of making a comparative study, other methods of charging a room were tried and determinations of the yield of formaldehyde made. The following methods were tried: the autoclave, Trenner-Lee retort, Kühn lamp, and the "sheet-spraying method."

Evans, in the article cited above, states that "all determinations of the amounts of formaldehyde were made by Romijn's potassium cyanide method,<sup>2</sup> as experience showed that this method is capable of yielding better results than the iodine

<sup>1</sup> "Formaldehyde Disinfection," 13th Ann. Rep., State Board of Health of Maine.

<sup>2</sup> *Z. anal. Chem.* 36, 18 (1897); Smith: *This Journal*, 25, 1028 (1903).

methods." The method of experimenting is not described. In a letter received after my experiments were under way, Evans states that he "is at present engaged with the analysis of the gas in closed rooms, drawing measured portions of the air through cyanide and iodine solutions." It would seem from this that he had not obtained the percentage yield which he claimed for his method of liberating formaldehyde gas from formalin by examination of the air in a room. In my experiments the high yield which Evans gives in his article, namely, about 80 per cent., was by no means obtained.

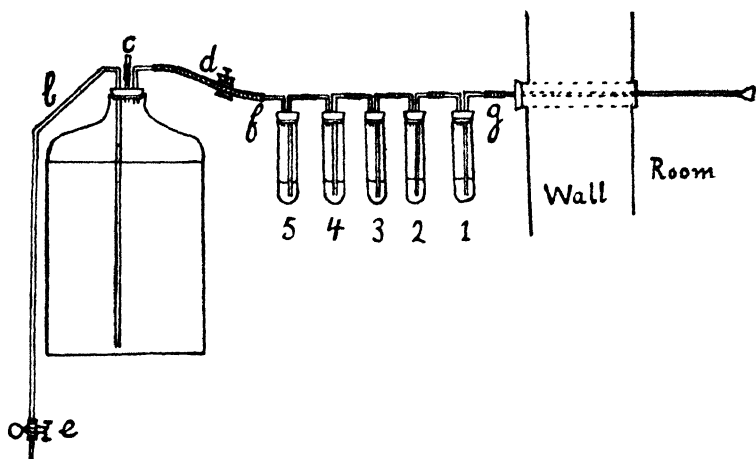
#### DESCRIPTION OF APPARATUS AND METHOD OF PROCEDURE.

The room into which the gas was liberated contained 2,000 cubic feet of space and was lined on the sides and ceiling as well as on the floor with sheet zinc, which overlapped the frames of the windows and doors. There were two well-fitting windows on opposite sides and two doors on the other two opposite sides. One of the doors had a small pane of glass inserted into it through which a view into the room was possible at all times. The wall containing this door was pierced by three parallel rows of zinc tubes about two inches in diameter and closed by rubber stoppers. The joints between the inner ends of the tubes and the wall of the room were made air-tight. The tubes of the middle row, which were about midway between the floor and ceiling and about six feet from the former, were used for drawing air from the room. For this purpose an ordinary glass tube about three feet long, to the end of which a small funnel was fitted, was passed through the rubber stopper and allowed to project outside the room about three inches. This end was joined by a rubber connection with a series of five thick-walled test-tubes about  $7 \times \frac{3}{4}$  inches, fitted with alternating long and short connecting glass tubes. The lower end of each long tube was tapered to a small orifice. For purposes of reference we may call these tubes 1, 2, 3, 4 and 5, tube 1 being next to the room.

The tubes contained the absorbing medium through which the air of the room was drawn by means of a partial vacuum. A large graduated bottle holding 20 liters of water, fitted with an inlet tube, a siphon tube, and an air tube was used for this purpose. The whole arrangement is shown in the figure below.

When everything was ready connection was made at *g* and *f*,

the screw-cock *d* was closed, the siphon *b* started by opening the pinch-cock *e*, and water allowed to flow until the level in the bottle was exactly on the upper line of the graduation, at which moment the cock *e* was closed; then the glass plug *c* was inserted.



The apparatus was now ready for starting the experiment. It is needless to say that the bottle, with all its tubes, up to the point *d* was tested for leaks. All rubber joints were tied before the experiment was started and tight-fitting rubber stoppers were used in tubes 1, 2, 3, 4 and 5.

To begin the experiment cock *e* was opened, whereby water flowed out until a certain partial vacuum was reached in the bottle, when it ceased. Then *d* was opened cautiously and the rate of bubbling of the air from the room through the tubes 1, 2, 3, 4, and 5 was so regulated that 10 liters of air required about one hour and fifteen minutes; this rate is easily secured after a few trials. As soon as the air began to bubble, the water started to run again from the siphon tube *e*. The flow was continued until the level in the bottle had reached the desired mark of the graduation, when cock *e* was closed. Air continued to bubble until the partial vacuum in the bottle was reduced.

In order to make the conditions of pressure as nearly as possible like those in the apparatus at the beginning, the long tubes in 1, 2, 3, 4, and 5 were drawn up until the orifices were just below the surface of the liquid. This caused more air to bubble through the tubes. The volume of air drawn from the room is measured by



the volume of water that flowed from the bottle between the two marks of graduation. Finally tube 1 was disconnected at *g* and tube 5 at *f*. The series of tubes was then removed for titration.

#### SOLUTIONS AND TITRATION.

As the quantity of formaldehyde in a relatively small proportion of the air (say 10 liters) of the room was small, it was decided to use the potassium cyanide method of titration and also to use a solution of potassium cyanide as absorbing medium. The cyanide method is admitted to be accurate for small quantities of the aldehyde.

*Potassium Cyanide Solution.*—This was made by dissolving 3.3 grams of the salt (purity of 96 per cent. or over) in water; the volume was made up to 500 cc. The solution was standardized in the usual way against an excess of a decinormal solution of silver nitrate acidified with 4 or 5 drops of concentrated nitric acid, the excess of silver solution in the filtrate being determined by a standard sulphocyanate solution with iron alum as indicator.

In the titration of a dilute formaldehyde solution a definite volume or weight (known not to be in excess) is added to 10 cc., or more if necessary, of the standard potassium cyanide solution. The latter, after stirring, is added to an acidified excess of decinormal silver nitrate solution, the whole made up to 100 cc. or 200 cc., and the excess of silver in 50 or 100 cc. of the clear filtrate titrated with sulphocyanate. From the amount of sulphocyanate required the volume of silver nitrate precipitated by potassium cyanide is calculated, and the difference between this and the volume of silver nitrate equivalent to the amount of cyanide solution originally taken is the number of cubic centimeters of silver solution that represents the formaldehyde present; this number of cubic centimeters multiplied by 0.003 (more correctly 0.00298) gives the weight of absolute formaldehyde,  $\text{HCOH}$ .

The silver cyanide precipitate must be removed before titrating an excess of silver by sulphocyanate, because it interferes with the sharpness of the end-point and causes error.

As stated in the foregoing, potassium cyanide solution was chosen as the medium for absorbing the formaldehyde gas in the air of the charged room. It was soon discovered that the air bubbling through the solution carried away a little hydrocyanic acid. To avoid loss of the latter the last tube containing the

cyanide solution was followed by one containing silver nitrate solution, which effectually precipitated all the hydrocyanic acid carried over into it. The silver nitrate tube was followed by one containing distilled water. This tube showed no trace of hydrocyanic acid when tested by the ferric ferrocyanide reaction, and no formaldehyde when tested by Schiff's fuchsin-bisulphite reagent,<sup>1</sup> or ammonio-silver nitrate solution.

In preliminary experiments the contents of the silver nitrate tube, after formaldehyde-laden air had been drawn through the series, was tested for formaldehyde to determine if any had escaped absorption in the cyanide tubes. To some of the liquid, about 2 cc. of Schiff's reagent were added; a precipitate of silver chloride was produced, but no pink or purple color, thus indicating the absence of formaldehyde. For comparison the reagent was also added to a few cubic centimeters of silver nitrate solution to which had been added a trace of formaldehyde; the contents of the tube soon acquired a pink color. It seemed evident that formaldehyde is wholly absorbed from air passing through a series of tubes containing cyanide solution. This conclusion was further strengthened by experiments on the absorption of formaldehyde from air by water alone.

After nearly all the results given further on had been obtained by the cyanide method, there came to my notice an article by Trillat<sup>2</sup> in which the author states that formaldehyde can be completely absorbed from air by passing it through a sufficient number of absorption tubes containing water alone. This suggestion was put to the test and it was found that three water tubes absorbed all of the formaldehyde, the last tube containing only a trace. My reason for not having chosen water at the start as an absorbing medium was that I supposed a solution containing a substance, as cyanide, which combines chemically with formaldehyde would be better suited than pure water as an absorbing agent. Owing to circumstances, it was not possible for me to repeat all of the experiments and use water tubes to absorb the formaldehyde, but in several instances the absorption

<sup>1</sup> Schiff's reagent: This is prepared by adding 20 cc. of a solution of sodium bisulphite (sp. gr. 1.27) to 1000 cc. of aqueous fuchsin solution (1:1000), and, after one hour, adding 10 cc. of pure concentrated hydrochloric acid. It should be preserved in a well stoppered bottle.

<sup>2</sup> Trillat, A.: "Présence normale de la formaldéhyde dans les produits de la combustion incomplète," *Rev. Hyg.*, Vol. 27, No. 2, Feb. 20, 1905.

from the same charged air of the room was carried out in cyanide tubes and in water tubes, side by side. Although three tubes are sufficient, five tubes of water were used for greater certainty. In these parallel experiments the percentage results in the case of absorption by water were practically the same as those in the case of absorption by cyanide. On examining the literature before putting my results together, I found von Brunn's article, in which he determined formaldehyde by drawing the charged air through water. von Brunn used in his determinations 3 Drechsel gas wash-bottles, each containing 100 cc. of water and aspirated 20 liters of air in twenty to thirty minutes. This would have been a too rapid rate for the volumes of liquid used in the absorbing tubes in my experiments, in which the rate of aspiration was from one-fourth to one-fifth as fast as in von Brunn's experiments. He found that nearly all of the formaldehyde was absorbed in the first bottle, the third one containing practically none.

DETAILS AS TO QUANTITY AND MANIPULATION IN THE DETERMINATION OF FORMALDEHYDE IN THE AIR OF THE CHARGED ROOM.

To give the figures involved in obtaining each result tabulated below would needlessly increase the length of this paper, but to give an idea of quantities of reagents used and method of carrying out the titration one experiment will be described in full.

Tube 1 contained about 8 cc. KCN solution.

Tube 2 contained about 5 cc. KCN solution.

Tube 3 contained 2 cc. KCN solution.

Tube 4 contained about 8 cc. N/10  $\text{AgNO}_3$  solution.

Tube 5 contained about 10 cc. distilled water.

Only the total quantity of cyanide need be measured, which, in this case, was exactly 15 cc., distributed about as stated. There should be not less than 8 or 9 cc. of cyanide solution in the first tube, lest there be an excess of uncombined formaldehyde in the liquid at the end of the absorption. Distilled water was added to the three cyanide tubes to make the column of liquid about 1.5 inches high, and to the silver nitrate tube to make a column about 1 inch high. The tubes were connected and air drawn through them as described above.

Volume of air drawn from room was 10 liters.

Time required to draw air was one hour, four minutes.

The five tubes were disconnected. Seven cc. of  $N/10$   $AgNO_3$  solution were introduced into a 250 cc. flask and 8 or 10 drops of strong nitric acid added, then through a funnel, the silver nitrate solution in tube 4 and its connecting tubes was carefully rinsed into the flask, followed in like manner by tubes 1, 2 and 3. The flask was then filled to the graduation mark with water and the contents thoroughly shaken. One hundred cc. of the clear filtrate were titrated for excess of silver nitrate; 1.4 cc. of potassium sulphocyanate solution were required.

Ten cc. KCNS solution = 10.21 cc.  $N/10$   $AgNO_3$ .

Ten cc. KCN solution = 9.64 cc.  $N/10$   $AgNO_3$ .

By calculation the formaldehyde absorbed from the 10 liters of air corresponded to 3.03 cc.  $N/10$  silver nitrate solution, which represents  $3.03 \times 0.003 = 0.00909$  gram of formaldehyde. One cubic foot of the air (28.315 liters) contained 0.0257 gram of formaldehyde.

The quantity of formalin used to charge the room in nearly all the experiments, tabulated further on, was 600 cc. of 35.66 per cent. by volume; *i. e.*, 100 cc. of the formalin contained 35.66 grams of absolute formaldehyde. The strength was determined by the Blank and Finkenbeiner method of titration with hydrogen dioxide and caustic soda solutions.<sup>1</sup> The formalin was taken from the same supply in all the experiments.

In the experiment just described 600 cc. of formalin were used to charge the room. The results may be expressed in percentage, based on the amount of absolute formaldehyde taken per cubic foot of space in charging the room. The weight per cubic foot is

$$\frac{600 \text{ cc.} \times 0.3566}{2000} = 0.107 \text{ gram HCOH.}$$

$$\text{The percentage would be } \frac{0.0257 \times 100}{0.107} = 24.01.$$

From von Brunn's determinations, the question would seem to arise whether in my experiments the amount of formaldehyde found in the air of the room really represented all the formaldehyde in the room. To make this clear, it will be necessary to state the results of von Brunn's experiments. He first showed that when diluted solutions of formaldehyde are distilled from flasks, no paraformaldehyde is formed in the distillate or the

<sup>1</sup> For description, see original article in Ber. 31, 2979, or the U. S. Pharmacopoeia, 8th decennial revision, or Sutton's "Volumetric Analysis."

residue, as far as could be judged by the absence of cloudiness in the liquids when cooled, and that the sum of the amounts of formaldehyde found in the distillate and residue was practically equal to the amount of formaldehyde present before distillation. The concentrations of the solutions distilled ranged from 21.5 to 4.35 per cent. He states that paraformaldehyde is formed only when the concentration of a solution rises above 40 per cent. during distillation, but that with diluted solutions, for example 20 per cent. or less, there is little tendency for the per cent. to rise in the residue in the flask during distillation.

von Brunn next proceeded to make distillations from the "Breslau still" devised by C. Flügge,<sup>1</sup> of Breslau. This still has a large heating surface and relatively small outlet so that the pressure rises to 29 cm. of water (about 2.1 cm. of mercury). In two distillations of diluted formalin and determination of the formaldehyde in the distillate and residue, there was a loss of about 2 per cent., which was accounted for by the collection of some paraformaldehyde in the tube of the condenser. When this was titrated, it made up the difference. von Brunn attributed the formation of the small quantity of paraformaldehyde to the increase of pressure in the Breslau still as compared with that in the case of distillation from glass flasks.

Having thus a means of knowing pretty closely how much formaldehyde entered a room by determining how much remained in the residue in the still, von Brunn determined the amount of formaldehyde in the air of a charged room, in the manner already stated. He made three determinations, and the highest amount obtained was 16.94 per cent. of the total weight of formaldehyde introduced into the room. He worked with approximately 8 per cent. solutions, and in the experiment just mentioned, 2990 cc. of liquid, containing 255.6 grams of formaldehyde, were evaporated into a room of 2824 cubic feet. A piece of filter-paper hung up in the room and removed half an hour after the charging was finished, was found to have absorbed formaldehyde at the rate of 1.236 grams per square meter of surface. The conclusions at which von Brunn arrived may be interesting to some who are concerned with disinfection by formaldehyde and they are therefore given here. "It can be said

<sup>1</sup> Flügge: "Die Wohnungsdesinfection durch Formaldehyd," *Z. Hyg. und Infectiouskrankheiten*, 29, 276 (1898).

that the greatest portion of the liberated formaldehyde is condensed at once on the surface of the walls and on the objects in the room. Accordingly the idea that in disinfection the formaldehyde acts as a gas needs correction. The more experiments have been made with formaldehyde, the more has it been observed that its maximum germicidal effect can only be attained in the presence of an abundance of water vapor. Therefore it appears that, by vaporizing formaldehyde, we only accomplish a uniform distribution of the disinfectant in space, but that the real efficacy lies not in the formaldehyde gas, but in the solution which condenses everywhere on surfaces."

von Brunn and all others who used the Breslau method of Flüge to charge rooms made it a point to bring the moisture up to or very nearly to the saturation point, under which conditions formaldehyde will no doubt be condensed upon objects ordinarily present in rooms much more readily than when the moisture is short of saturation. In my experiments the air of the room became saturated with moisture in only one case, namely, in charging with the Kühn alcohol lamp; moreover, there were no objects in the room and the only surfaces exposed to the formaldehyde gas that were not zinc-lined, were those of the glass windows and their frames. It is not probable that any considerable amount of formaldehyde was condensed on the zinc walls of the room. In fact there is good reason for believing that there was practically no condensation, because determinations made on the total amount of formaldehyde charged into a large glass bottle (24 liters) by the permanganate-formalin method on a reduced scale, agreed fairly well with those made on the air of the large room charged by the same method. Had there been such loss of formaldehyde from the air of the room by condensation upon the walls as von Brunn states, the results just referred to would never have approximated as closely as they did. The results of the determinations of the formaldehyde charged into the glass bottle are given in Tables 6 and 7.

Von Brunn did not state what the conditions were in the room which he charged, but it is probable that it was an ordinary one and contained the objects usually present, such as chairs, table, clothing, etc. In fact most experimenters have purposely left such objects in rooms in order to have conditions very nearly like those in living rooms when about to be disinfected.

Axel Jörgensen<sup>1</sup> found that paper, cloth, etc., condense formaldehyde from moist air laden with it, and that a room with wooden walls, having been charged and then ventilated for several days until the odor had vanished and closed again for more than a month, had developed such an odor of formaldehyde when opened that one could not endure remaining in it. He concludes that the total surface of walls in rooms is important, and that proportionately more formaldehyde should be introduced when there is a large wall-surface to compensate for the greater condensation and thus leave the same amount of gas in the air as would be present in a smaller room with less condensation. This point has also been brought out by Peerenboom, Walter and Schlossmann, and Werner. Jörgensen recommends for disinfection purposes rooms with walls of stone, glass, or metal.

If von Brunn's experiments were made in an ordinary room with objects in it and walls of absorbing material, the small percentage of the total formaldehyde introduced that he found in the air of the room can readily be accounted for. In my experiments it seems quite certain for the reasons given above that the amount of formaldehyde found in the air actually represented the whole amount of formaldehyde in the room at the time, or in other words condensation of formaldehyde upon the zinc walls did not occur.

As already stated, the windows and doors of the room into which the charges of formaldehyde were introduced, were tight-fitting, more so than those of the average living room, yet the room was not perfectly air-tight. Therefore the results recorded further on do not represent the total amount of formaldehyde that left the charging apparatus, but rather the average amount present in the room during the time of the determination and after a certain interval from the time the charging was finished. On a quiet day the rate of leakage was relatively small as is shown by the results, so that the amount of formaldehyde found on such a day soon after the charge was introduced must be fairly close to what would have been found if the room had been perfectly air-tight. In a few experiments, the window-frames and cracks of the doors

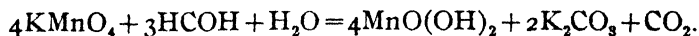
<sup>1</sup> Jörgensen: "Untersuchungen über Formaldehyddesinfection nach der Breslauer Methode,—speciell Desinfection von Uniformen betreffend," *Z. Hygiene und Infectiönskrankheiten*, 45, 237 (1903).

were covered by pasting on heavy smooth paper, but the amount of formaldehyde found was only a little larger than when the paper was omitted; this would seem to show that the rate of leakage from the room was small.

PERMANGANATE-FORMALIN METHOD OF CHARGING THE ROOM,  
PROPOSED BY EVANS AND RUSSELL.

When formalin is poured upon crystals of potassium permanganate a vigorous action takes place after a few seconds, accompanied by a strong ebullition of the liquid and sufficient heat to produce a large quantity of steam. The reaction is apparently over in a comparatively short time (about five minutes) and with proper proportion of substances, the residue in the vessel is almost dry. The heat produced by the action of the permanganate on a portion of the formaldehyde is sufficient to evaporate nearly all the remainder.

The exact nature of the chemical reaction that takes place was not investigated as for the purposes of the experiments the fact of main interest was that an abundance of formaldehyde is given off in gaseous form. According to Evans and Russell, "analysis of the gas thrown out into a room by this reaction showed it to consist of formaldehyde, water vapor, carbon dioxide, and a very small amount of formic acid. In the generator were found a lower oxide of manganese, a little formaldehyde, carbon dioxide, potassium hydroxide, and, I think, a little potassium formate resulting from the neutralization of the potassium hydroxide by formic acid." It seems highly probable that the decomposition takes place essentially according to the following reaction:



In accordance with this reaction about one-fifth of the formaldehyde is destroyed. The reaction is of value, of course, only because it furnishes the heat necessary to vaporize the rest of the formaldehyde.

Evans and Russell used the ratio of 100 cc. of formalin to 37.5 grams of permanganate, but it was found in the present experiments that with this proportion considerable formalin remained in the residue in the generator, as was evidenced by its wet condition and powerful odor of formaldehyde. After some experimenting the ratio of 100 cc. of formalin to 50 grams of permanganate was adopted; this gave a residue fairly free from liquid.



The quantity used to charge the room of 2,000 cubic feet was in nearly all cases 600 cc. formalin (35.66 per cent. by volume). The generator was a galvanized iron pail 10 inches wide and 10 inches high holding 12 liters (3 gallons). The ebullition was so vigorous that the frothy mass often reached nearly to the top of the pail. The pail was placed in the center of the room, the permanganate dropped into it, the formalin poured quickly upon it, and a hasty exit made from the room.

The action is more rapid, the more finely powdered are the permanganate crystals; in the experiments to follow, the small needle crystals of commerce were used without further powdering.

Many variations of conditions might have been tried, such as covering the pail with sheet asbestos to retain the heat, or heating the pail before the experiment, or placing it in hot water, or powdering the permanganate crystals, etc., but as time was a factor it was thought best to adopt those conditions which would be least cumbersome to execute by public officers or others in disinfecting rooms.

In the experiments (Table I) the ratio of the quantities used was 100 parts by volume of formalin to 50 parts by weight of permanganate, and approximately fifteen minutes were allowed to elapse between the time of mixing these and the beginning of drawing the air through the absorption tubes. This seemed sufficient time for the action to cease and for the formaldehyde gas to diffuse through the air of the room. The relative humidity in the room before and after charging was determined by means of a dry and wet bulb thermometer, which was so arranged that it could be swung around in the room and the results observed by the operator through a pane of glass in the door. By means of tables the grains of moisture per cubic foot were calculated. Before a new charge was put into the room all formaldehyde of the previous one was gotten rid of by opening the door and windows until no odor was perceptible.

*Comments.*—Although the room in which the experiments were made was zinc-lined and the doors and windows were fairly close-fitting, yet it was not air-tight, so that the conditions were not of that exact quantitative character which obtains in an operation like the precipitation of sulphuric acid by barium chloride. In view of this fact, although the percentages vary by several units, they can be considered as agreeing fairly well. In III, where the

TABLE I.—EXPERIMENTS WITH PERMANGANATE AND UNDILUTED FORMALIN.

	Date and temperature of room before experiment	Formalin (35.66 per cent. by volume) cc.	KMnO <sub>4</sub> . Grams.	Time between mixing and drawing air.	Time required to draw air	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity ten minutes after mixing.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I. 6/27, '05. 71° F.		600	300	a. 14 min. b. 3 hrs. 38 min.	1 hr. 10 min. 1 hr. 21 min.	10	72	86	1.47	0.107	0.0403	37.79	Moderate wind.
II. 6/28, '05. 69° F.		800	400	a. 12 min. b. 22 hrs. 17 min.	1 hr. 32 min. 1 hr. 10 min.	10	63	86	2.0	0.1426	0.0505	35.41	Slight breeze.
III. 6/30, '05. 77° F.		400	200	15 min.	1 hr. 12 min.	11	79	85	0.58	0.1426	0.0172	12.07	Very slight breeze.
IV. 7/24, '05. 79° F.		600	300	17 min.	1 hr. 21 min.	10	79	94	1.72	0.0713	0.025	35.06	Moderate wind.
										0.107	0.0419	39.15	Practically no wind. Windows and doors of room pasted up.

room was made more nearly air-tight by pasting paper over the cracks of the door and covering the window frames, the per cent. is a little higher. These experiments also indicate that the relation between the formalin and permanganate in the ratio taken is fairly quantitative and that the percentage yield of formaldehyde gas is approximately the same whether 400, 600 or 800 cc. be taken for a charge. Experiments I *b* and II *b* give an idea of the rate of leakage of formaldehyde from the room. In I *b*, the loss after an interval of about three and one-half hours was  $\frac{2}{5}$  of the formaldehyde, in II *b* it was about  $\frac{3}{5}$  after an interval of twenty-two hours.

It is probable that on a very quiet day after fifteen or twenty minutes with a charge of 600 cc. formalin (35.66 per cent. by volume) the weight of the gas in the room would be at least between 38 and 39 per cent. of the weight in the 600 cc. of formalin taken, and in a room with fairly tight windows and doors.

#### EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

A number of experiments were made with formalin diluted with various quantities of water, and with different weights of permanganate.

A fixed volume of formalin was taken (600 cc.) and the interval between setting off the charge and beginning to draw air, the volume of air drawn (10 liters), and the time required to draw it were about the same as in Table I. In several instances two experiments were made simultaneously with 5 and 10 liters of air respectively.

*Comments.*—Of the various proportions used that of 600 cc. formalin, 300 cc. water and 375 grams of permanganate gives the highest yield of formaldehyde gas.

In Experiment I the determinations *a* and *b*, made simultaneously and on the same volume of air, gave the same results, which would seem to indicate that the method of analysis, under the same conditions, gives constant results. In Experiment III, 5 liters of air in *a* were drawn in the same time as 10 liters in *b* with practically the same result, which seems to point to the conclusion that 5 liters of air is a large enough quantity for a determination.

In Experiments IV, V, VI and VII the same proportion of materials were used to charge the room, but the results in IV are

TABLE II.—EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.														
	Date and tempera- ture of room before experiment.	Formalin (35 66 per cent by vol- ume). cc.	Water. cc.	KMnO <sub>4</sub> . Grams.	Time between mixing and drawing air.	Time required to draw air.	Volume air drawn in liters.	Relative humidity before experi- ment.	Relative humidity ten minutes after mixing	Increase in grains of moisture per cubic foot.	Absolute formal- dehyde taken per cubic foot. Gram.	Absolute formal- dehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I. 7/3, '05. 81° F.	600	600	450	17 min.	<i>a.</i> 1 hr. 20 min. <i>b.</i> 1 hr. 20 min.	10	81	94	1.79	0.107	0.0272	25.4	Slight breeze.	
II. 7/10, '05. 81° F.	600	300	450	16 min.	1 hr. 5 min.	10	83	98	2.06	0.107	0.0272	25.4	Slight breeze.	
III. 7/11, '05. 81.5° F.	600	300	300	16 min.	<i>a.</i> 1 hr. 9 min. <i>b.</i> 1 hr. 8 min.	5	74	94	2.28	0.107	0.0242	22.6	Moderate wind.	
IV. 7/12, '05. 81° F.	600	300	375	14 min.	<i>a.</i> 45 min. <i>b.</i> 1 hr. 14 min.	5	77	96	2.14	0.107	0.02336	21.8	Moderate wind.	
V. 7/17, '05. 85° F.	600	300	375	15 min.	<i>a.</i> 34 min. <i>b.</i> 1 hr. 5 min.	5	70	90	2.55	0.107	0.02965	27.7	Brisk wind.	
VI. 7/18, '05. 85° F.	600	300	375	<i>a.</i> 17 min. <i>b.</i> 17 min.	<i>a.</i> 42 min. <i>b.</i> 1 hr. 20 min.	5	70	88	2.3	0.107	0.0341	31.84	Gentle breeze.	
Cont'd 7/19, '05. 79° F.	600	300	375	<i>c.</i> 2 hrs. 27 min. <i>d.</i> 4 hrs. 24 min. <i>e.</i> 24 hrs. 33 min.	1 hr. 18 min. 1 hr. 1 hr. 23 min.	10	79	94	1.72	0.107	0.03296	30.80	Gentle breeze.	
VII. 7/21, '05. 79° F.	600	300	375	<i>a.</i> 21 min. <i>b.</i> 21 min.	47 min. 1 hr. 17 min.	5	79	94	1.72	0.107	0.03517	32.87	Practically no wind.	
Cont'd 7/22, '05.				<i>c.</i> 4 hrs. 7 min. <i>d.</i> 23 hrs. 46 min.	1 hr. 18 min. 1 hr. 13 min.	10				0.107	0.02658	24.84	windows and doors pasted up with stout smooth paper.	

low on account of the brisk wind blowing at the time, and should not be compared with those of V, VI and VII. The three determinations of V, VI and VII which are comparable show a fairly close agreement. VI and VII show the rate of leakage from the room, the loss of formaldehyde in VI in two, four and twenty-four hours after the first determination being about  $2/10$ ,  $3/10$  and  $7/10$  respectively, in VII after four and twenty-three and one-half hours being about  $25/100$  and  $56/100$  respectively,  $d$  and  $e$  of VI and  $c$  and  $d$  of VII, which are comparable, show that when there is very little wind the leakage from the room when pasted up with paper is not much less than when it is not pasted. V  $a$  seems to be abnormally high when compared with VI  $a$  and VII  $a$ .

With the proportions of 600 cc. formalin (35.66 per cent.), 300 cc. water and 375 grams potassium permanganate, it is probable from the results that after fifteen or twenty minutes on a quiet day in a tight room the amount of formaldehyde gas obtained would be approximately 32 per cent.

The addition of water to the formalin has the effect of increasing the amount of moisture sent out into the room which probably would offset in disinfection the lower per cent. of formaldehyde obtained than in the case of undiluted formalin, since it is claimed by many that high relative humidity is an important factor in the action of formaldehyde gas upon bacteria.

#### CHARGING THE ROOM BY THE AUTOCLAVE.

Six hundred cc. of formalin, 60 cc. of glycerol, 120 grams of calcium chloride, and water sufficient to make a volume of 1000 cc. constituted the charge for each experiment. The pressure was raised to between 50 and 60 pounds, when the cock was opened and injection continued till the pressure had fallen to about 20 pounds. Then the pressure was raised and vapor again injected.

This process was repeated until the pressure rose very slowly and vapor almost ceased to escape from the nozzle of the autoclave, which was inserted through a suitable hole in the door. After each experiment there was little liquid left in the autoclave.

*Comments.*—From the result of III  $a$  it seems probable that on a calm day in a fairly tight room the amount of formaldehyde by the autoclave from 600 cc. of formalin would be approximately 42 per cent. after an interval of about thirty minutes from the time of removing the nozzle from the room.

TABLE III.—EXPERIMENTS WITH THE AUTOCLAVE.

Date and temperature of room before experiment.		Time required to exhaust autoclave		Time between beginning of discharge to drawing of air.		Time required to draw air.		Volume of air drawn in liters.		Relative humidity before experiment.		Relative humidity five minutes after removing autoclave.		Increase in grains of moisture per cubic foot.		Absolute formaldehyde taken per cubic foot. Gram.		Absolute formaldehyde found per cubic foot.		Yield. Per cent.		Condition of wind.	
I.	6/23, '05. 80° F.	25 min.		3 hrs. 32 min.		1 hr. 18 min.		10		75		96		2.96		0.107		0.0406		37.94		Almost no wind.	
II.	6/26, '05. 81.5° F.	25 min.	a. 35 min. b. 3 hrs. 33 min.			1 hr. 17 min. 1 hr. 4 min.		10		81		94		2.00		0.107		0.04213		39.37 20.18		Good breeze. Storm.	
III.	7/15, '05. 80° F.	22 min.	a. 40 min. b. 1 hr. 41 min.			1 hr. 10 min. 1 hr. 20 min.		11		75		94		2.23		0.107		0.04448 0.04116		41.57 38.46		Almost no wind. Almost no wind.	

II *a* is lower than III *a*, which was to be expected because of the stronger wind blowing.

II *b* shows the rapid loss of formaldehyde gas during a strong wind or storm. During the time the air was drawn in this experiment a severe thunderstorm was in progress, with the result that during the interval of three hours between *a* and *b* nearly half the formaldehyde escaped from the room.

Apparently over half the formaldehyde gas in the 600 cc. of formalin used to charge the air was lost. It is altogether improbable that the most of this escaped from the room during the twenty-five minutes required to exhaust the autoclave, as is evident from the slow rate of loss on a calm day shown in I and III *a* and *b*. It is more probable that under the high temperature and pressure in the autoclave the formaldehyde undergoes change. It would be an interesting problem to work out the fate of the lost formaldehyde. The mixture of formalin, glycerol and calcium chloride was devised by A. Trillat to prevent, as he asserted, the formation of paraformaldehyde. If the results in my experiments represent the amount of formaldehyde injected into the room, and there seems to be no strong reason to think the contrary, then there is a loss of formaldehyde somehow in the autoclave. There are two plausible views, either that the formaldehyde is partly decomposed, or polymerized, or perhaps both.

#### CHARGING THE ROOM BY THE TRENNER-LEE RETORT.

The formalin in this method is simply heated to the boiling-point under atmospheric pressure in a retort and the issuing water vapor and formaldehyde gas are passed into the room through a suitable tube.

In the following experiments 600 cc. of formalin to which were added 6 cc. of glycerol were taken for the charge, and the heat was continued under the retort until vapor practically ceased to issue from the outlet tube. When the retort was removed there was little liquid left in it.

*Comments.*—The yield of formaldehyde gas by this method was appreciably higher than by the autoclave method, although the time required to exhaust the apparatus was more than twice as long in the former as in the latter. Because of this longer time there was naturally more loss by leakage in this method before beginning to draw air. The higher percentage would be ex-

TABLE IV.—EXPERIMENTS WITH TRENNER-LEE RETORT.

I. 7/27, '05. 73° F.	1 hr.	Date and temperature of room before experiment.		Time required to exhaust retort.	Time between removal of retort and drawing air.	Time required to draw air.	Volume of air drawn in liters	Relative humidity before experiment.	Relative humidity at end of injection.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot Gram	Yield. Per cent.	Condition of wind.
II. 7/28, '05. 76° F.	1 hr.	Date and temperature of room before experiment.		Time required to exhaust retort.	Time between removal of retort and drawing air.	Time required to draw air.	Volume of air drawn in liters	Relative humidity before experiment.	Relative humidity at end of injection.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot Gram	Yield. Per cent.	Condition of wind.
Cont'd 7/31.	1 hr.	Date and temperature of room before experiment.		Time required to exhaust retort.	Time between removal of retort and drawing air.	Time required to draw air.	Volume of air drawn in liters	Relative humidity before experiment.	Relative humidity at end of injection.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot Gram	Yield. Per cent.	Condition of wind.



pected, since in the retort the formaldehyde is not subjected to as high a temperature and pressure as in the autoclave. Although the yield was greater in the retort method than in any other tried, there arises the question as to what becomes of the rest of the formaldehyde. In view of von Brunn's experiments, it seems probable that some of the formaldehyde was polymerized to paraformaldehyde the greater part of which perhaps remained in the retort. It is also likely that some paraformaldehyde entered the room, although there was nothing in the appearance of the room atmosphere to indicate this. The atmosphere was clear.

Experiments II *a* and *b* show the slow rate of leakage from the room on a quiet day, the loss in an interval of three hours and twenty minutes being about  $3/20$  of the amount found in *a*. I and II agree very closely, the difference being only about 1 per cent. From I and II, it seems probable that on a quiet day in a tight room the amount of formaldehyde gas present by this method after an interval of twenty minutes from removal of the retort would be approximately 47 per cent.

In regard to the question of the formation of paraformaldehyde when formalin is heated, most contradictory statements are found in the literature. Novy and Waite<sup>1</sup> assert the following: "The fear of polymerization of formalin on boiling is not well grounded. Certain it is that formalin can be distilled from its aqueous solution without polymerization, and that the results obtained are in every way equal to those obtained from paraform and decidedly superior to the so-called formalin lamps." "The statement is freely made that formaldehyde solutions cannot be heated without polymerization and thus interfering with further evaporation. Formalin, if heated slowly in an open dish, may possibly polymerize, especially when concentrated to about 25 cc., but we have never found this to take place when the formalin solution was rapidly heated in a glass flask or copper container." On the other hand von Brunn in the article cited, which was published a year later, stated that when formalin of about 32 per cent. or more was distilled from a glass flask, the residue in the flask upon cooling became cloudy or opaque, indicating paraformaldehyde. Only when diluted solutions, 20 per cent. or less, were distilled, was there no paraformaldehyde formed. Novy and Waite had used

<sup>1</sup> "The Disinfection of Rooms," *Med. News*, 72, 641 (1898).

an approximately 40 per cent. solution. The loss of formaldehyde as indicated in my determinations seems to point to the formation of paraformaldehyde in the retort and to the correctness of von Brunn's statements.

#### SHEET-SPRAYING METHOD.

Two sheets, about 8 x 5 feet were hung up in the room in a slanting position at an angle of about 45°. It was found advantageous to have them just damp to the touch when hung up, as the formalin was absorbed by the fibers more quickly and had very little tendency to run off the sheet. Six hundred cc. of formalin were sprayed uniformly and the door closed. About one and one-half hours were allowed for the formaldehyde to diffuse before beginning to draw air. The sheets were washed before the next spraying.

*Comments.*—Compared with the previous methods this one produces a fairly good quantity of formaldehyde gas in the air of the room. The results show that the quantity increases during a relatively long period of time. In Experiment II *c* the quantity of formaldehyde gas found after an interval of twenty-two hours was only 2.75 per cent. less than that found in II *a*, ninety minutes after closing the room.

Evidently, an advantage of this method is the fact that formaldehyde continues to be supplied to the air of the room for a long time, whereas, in the other methods, the per cent. of the gas begins to diminish by leakage from the moment the charging is finished.<sup>1</sup>

It is impossible to indicate the yield of gas in this method, as the gas is given off continuously for a long period. Moreover it is probable that on a dry day the amount of gas given off after a definite interval would be greater than on a very humid day, on account of slower evaporation in the latter case, and no doubt low temperatures would also have a retarding effect on the evaporation.

#### EXPERIMENT WITH THE KÜHN LAMP.

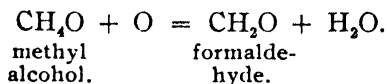
This is one of the various lamps devised for the purpose of generating formaldehyde by the partial oxidation of methyl

<sup>1</sup> The high degree of efficiency of this method, from the bacteriological side, has recently been emphasized by Ravenel and Gilliland, Univ. of Penn. Med. Bull. Vol. 16, p. 77.

TABLE V.—EXPERIMENTS WITH SHEET-SPRAYING METHOD.

Date and temperature of room before experiment.	Time between closing room and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity after closing room.	Gain in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot.	Gram. Absolute formaldehyde found per cubic foot.	Per cent.	Condition of wind.
I. 8/3, '05. 76.5° F.	a. 1 hr. 26 min.	1 hr. 13 min.	10	72	83 (after 5 hrs.)	1.6	0.107	0.02576	24.07	No wind.
	b. 3 hrs. 47 min.	1 hr. 8 min.	10				0.107	0.03262	30.48	No wind.
II. 8/4, '05. 78° F.	a. 1 hr. 40 min.	1 hr. 15 min.	10	83	85 (after 3 hrs.)	0.49	0.107	0.0252	23.55	Gentle breeze.
	b. 4 hrs. 5 min.	1 hr. 7 min.	10				0.107	0.0305	28.50	Gentle breeze.
Cont'd 8/5.	c. 23 hrs. 30 min.	1 hr. 17 min.	10				0.107	0.02225	20.80	No wind.

alcohol. In the Kühn lamp this is brought about by means of hot platinized asbestos, which has the power of causing the oxygen of the air and methyl alcohol vapor to combine according to the following reaction:



The platinized asbestos is heated by first burning some of the alcohol, after which the flame is extinguished. Alcohol continues to vaporize and the heat produced in the oxidation keeps up the temperature of the apparatus. The time usually allowed for the exhaustion of the lamp is about two hours.

One thousand cc. of common methyl alcohol were placed in the reservoir of the lamp and 1500 cc. of water in the basin around the reservoir. During the action of the lamp an abundance of moisture was formed, which condensed on the small glass pane in the door of the room.

In a previous experiment it was found necessary to have two silver nitrate tubes to absorb the hydrocyanic acid which was carried over from the cyanide absorption tubes by the air bubbling through them. This was no doubt due to the presence of a great excess of carbonic acid and perhaps a small quantity of formic acid.

While formaldehyde is formed by the action of the platinized asbestos in the Kühn lamp it is not the only product of oxidation, for the oxidation extends as far as the formation of carbon dioxide. It is known that formic acid is oxidized to carbon dioxide by platinized asbestos. Engels condemns the methyl alcohol lamps and states that about 90 per cent. of the alcohol is oxidized to carbon dioxide and water and that the vapors from the lamps contain from 3 to 5 per cent. of carbon monoxide.<sup>1</sup>

The presence of either carbon dioxide or formic acid in the air bubbling through the cyanide absorption tubes would cause the liberation of some hydrocyanic acid, which would be carried over. The precipitate in the first silver nitrate tube was somewhat larger than in the case of the other methods. The precipitate in the second silver nitrate tube did not appear until towards the end of the experiment.

<sup>1</sup> Engels: "Experimentelle Beiträge zur Wohnungsdesinfection mit Formaldehyd," Archiv. Hygiene, 49, 129-199 (1904).\*

Result: Began to draw air two hours after the lamp was started. Volume of air drawn, 10 liters. Time required, one hour, thirteen minutes. Condition of wind, gentle breeze.

Temperature of room before experiment, 79; relative humidity, 87.

Temperature of room two hours after starting lamp, 85; relative humidity, 98.

If the quantity of formaldehyde found be referred for comparison to the amount of absolute formaldehyde allowed per cubic foot in the other methods, where 600 cc. of formalin were taken to charge the room, it is equivalent to  $\frac{0.01096 \times 100}{0.107} = 10.24$  per cent.

*Comments.*—The quantity of absolute formaldehyde obtained from 1000 cc. of methyl alcohol is considerably less than that obtained from 600 cc. of formalin by any of the other methods. Because of this relatively small quantity and the cumbersomeness and unreliability of the lamp as a means of producing the gas it was not thought worth while to make further determinations. One merit which the Kuhn lamp has is that it produces more moisture in the air of the room than the other methods described.

*Conclusions.*—The results obtained must be interpreted as representing the quantities of formaldehyde gas that may be expected to be present in a room made not absolutely but fairly air-tight when charged with formalin by the various methods described, on a day of little wind and after a certain interval of time which varies with the method used. According to the quantity of formaldehyde yielded it seems fair to arrange the methods in the following order:

- (1) Trenner-Lee retort.
- (2) Autoclave.
- (3) Permanganate-formalin, 300 grams to 600 cc.
- (4) Sheet spraying.
- (5) Permanganate-diluted formalin in the proportions of 600 cc. formalin, 300 cc. water and 375 grams permanganate.
- (6) Kuhn lamp, using 1000 cc. methyl alcohol as against 600 cc. formalin in the other methods.

For simplicity and expedition, the permanganate-formalin method is preferable to all the others. Moreover, the quantity of formaldehyde gas can easily be increased by using more formalin, which only requires a larger pail, a piece of apparatus not very

difficult to obtain, and correspondingly more permanganate. If it is desirable or necessary to have a greater degree of humidity in the air than results from this method, that could easily be supplied from a simple tin or copper still.

Although the sheet spraying-method may not give at any time so high a percentage of the gas as the permanganate-diluted formalin method, it is placed before the latter, because in the spraying method the amount of gas is kept up for a long time, while in the diluted formalin method it is constantly diminishing and after five or six hours would be less than in the spraying method.

The experiments described were carried out at summer temperature, between 69° and 85° F. No attempt was made to determine if any solid paraformaldehyde was present along with the gaseous formaldehyde in the air of the room, but it is quite likely that none or very little was present, since the air of the room after charging was free from haziness.<sup>1</sup> Paraformaldehyde as such has no value as a disinfectant, but it has the same effect on potassium cyanide in titrations as the gaseous product.

It may not be out of place to add here the conclusions of a recent experimenter as to the "practical requirements for an effective formaldehyde disinfection."<sup>2</sup> (1) In all cases, an average of 5 grams of formaldehyde (absolute) per cubic meter of space (0.1416 gram per cubic foot) should be present, with seven hours' action. (2) In exceptional cases, where loss of formaldehyde can not be avoided, or where numerous objects or a good deal of matter of an organic nature which can not be

<sup>1</sup> M. B. Porch (assistant in Pharmacology, Hygienic Laboratory, Washington), using the same apparatus and methods that I did, but working at lower temperatures, found that polymerization of formaldehyde gas begins at about 62° F., and becomes more marked as the temperature decreases, which is evidenced by the persistent hazy condition of the air of the room, the low percentage yield of formaldehyde, and the deposition of paraformaldehyde in the room. He obtained in the permanganate-formalin method a yield of 25.1 per cent. at 62° F. and 11.1 per cent. at 52° F., as against 38.39 per cent. obtained by me at the higher temperatures of my experiments, namely, 71° and 79° F. He found similar results in the case of the autoclave method and that in the sheet-spraying method little formaldehyde is evaporated in cold weather and that polymerization takes place on the sheet.

<sup>2</sup> G. Werner: "Zur Kritik der Formaldehyddesinfektion," *Archiv. Hygiene*, 50, 305 (1904).

conveniently removed, are present in the room, the quantity of formaldehyde should be doubled. (3) In all cases, when the room temperature is below 50° F., it should be raised. 68-77° F. is an efficient temperature. (4) The strength of the formalin used should be known. Werner used the Breslau still in his experiments and saturated the air with moisture, using a hair hygrometer to determine the latter.

DETERMINATION OF FORMALDEHYDE CHARGED INTO A LARGE GLASS  
BOTTLE BY THE FORMALIN-PERMANGANATE METHOD, AND  
ALSO THE AMOUNT LEFT IN THE RESIDUE IN  
THE GENERATOR.

These experiments were carried out in two large bottles, one holding a trifle over 24 liters (0.85 cu. ft.), the other very nearly 18 liters (0.63 cu. ft.). The mouths of the bottles were 2.75 inches wide and were closed with tight-fitting corks, the pores of which were closed with melted paraffin.

A porcelain crucible holding 24 cc. was fitted into an excavated flat cork, which was suspended in a stirrup of thin twine.

The formalin was practically 40 per cent. by volume, as determined by the Blank and Finkenbeiner hydrogen dioxide method. In most of the experiments 0.7 cc. of this was used to charge the bottles; it was measured from a long slender pipette, in which 0.1 cc. made a column 1.7 cm. long. The method of procedure was as follows:

About 40 cc. of approximately decinormal potassium cyanide solution was measured from a burette into the bottle and about 50 cc. of water added. The liquid was then rolled over the side of the bottle to produce a greater absorbing surface. Then the crucible containing the formaldehyde was suspended in the mouth of the bottle, the permanganate dropped in from a piece of glazed paper, and the whole let down quickly into the bottle by a string and the cork securely placed. After a few seconds a vigorous action began, which seemed to be finished in about five minutes. About fifteen minutes, however, were allowed to elapse before the crucible was removed. This was done by slightly loosening the stopper, drawing up the crucible as near as possible to the stopper, removing the stopper for an instant, taking the crucible out, and then replacing the stopper. By repeatedly rolling the cyanide solution over the side of the bottle the formaldehyde was soon

absorbed (in about half an hour). When the odor of formaldehyde could no longer be detected, the contents of the bottle were transferred by thorough washing into a 500 cc. flask containing an excess of decinormal silver nitrate (about 10 cc.) acidified with nitric acid. The volume was made up to the graduation mark, the flask thoroughly shaken, and 250 cc. of the filtrate titrated with sulphocyanate solution, and calculation made as already described.

Method of procedure for the residue in the crucible. After the crucible was removed the contents were thoroughly extracted with water and filtered into a 250 cc. flask. The volume was made up to the graduation mark, and 50 cc. of the solution were added to about 15 cc. of the cyanide solution. After stirring, this was poured into an excess of acidified silver nitrate solution, which was stirred until the precipitate collected into a clot. The clear filtrate from the precipitate was then titrated with sulphocyanate solution for excess of silver.

*Comments.*—In all the experiments but the last two the ratio used was 1 part by volume of formalin to 0.5 part by weight of permanganate, the same as was used in the experiments of Table I. With this proportion the total amount of formaldehyde found in the air of the bottle and in the residue was fairly constant, considering the conditions of the experiments.

Evidently there is an advantage in using permanganate in powdered form, as is shown by comparing the results of IV, V, VI, VII and VIII with those of I, II and III. No doubt the reason for this is that action takes place more quickly with production of a higher temperature, so that more formalin evaporates from the crucible and less remains with the residue.

The results in Experiments I, II and III (average 33 per cent.) are lower than the results in Table I, which refer to experiments in charging the room of 2,000 cu. ft. This would be expected considering the small quantities used, whereby the quantity of heat produced is not so large, and the cooling of the generator is more rapid. In the experiments where powdered permanganate was used, the percentage yield is higher and in line with the results in Table I.

In Experiment IX, where only 0.5 cc. of formalin was used, the result is low; but this is probably due to the fact that the



## FORMALDEHYDE DISINFECTION.

TABLE VI.—RESULTS OF EXPERIMENTS IN GLASS BOTTLES.

	Date.	Size of bottle in liters	Formalin (40 per cent. by volume)	KMnO <sub>4</sub> Gram	Formaldehyde found in bottle Per cent.	Formaldehyde found in residue Per cent.	Total of formaldehyde found in bottle and residue Per cent.	Remarks.
I.	8/15, '05.	24	1	0.5	33.03	.....	.....	KMnO <sub>4</sub> in small needle crystals.
II.	8/16	24	1	0.5	33.52	38.25	71.77	KMnO <sub>4</sub> in small needle crystals.
III.	8/18	18	1	0.5	32.47	40.35	72.82	KMnO <sub>4</sub> in small needle crystals.
IV.	8/17	18	0.7	0.35	35.48	33.86	69.34	KMnO <sub>4</sub> ground to moderately fine powder.
V.	8/18	18	0.7	0.35	36.53	35.20	71.73	KMnO <sub>4</sub> ground to moderately fine powder.
VI.	8/18	24	1	0.5	.....	35.11	.....	KMnO <sub>4</sub> ground to moderately fine powder.
VII.	8/21	18	0.7	0.35	37.00	32.20	69.20	KMnO <sub>4</sub> ground to moderately fine powder.
VIII.	8/22	18	0.7	0.35	37.83	32.76	70.59	KMnO <sub>4</sub> ground to moderately fine powder.
IX.	8/19	18	0.5	0.25	33.28	38.10	71.38	KMnO <sub>4</sub> ground to moderately fine powder.
X.	8/25	18	0.7	0.4	34.37	25.16	59.53	KMnO <sub>4</sub> ground to moderately fine powder.
XI.	8/28	18	1	0.39	25.20	42.79	67.99	KMnO <sub>4</sub> ground to moderately fine powder.

quantity of formalin is too small to produce as vigorous an action as in the other cases.

In Experiment X the proportion of permanganate was increased, with the result that the amount of formaldehyde sent out into the bottle was not affected much, but considerably less remained with the residue.

In Experiment XI the permanganate was decreased to the ratio used by Evans (Maine Board of Health) in the report on his method. The result shows a considerable decrease in the formaldehyde sent out into the bottle and large increase in the amount remaining in the residue.

#### EXPERIMENTS WITH DILUTED FORMALIN AND PERMANGANATE.

Two experiments were made with 0.6 cc. formalin diluted with 0.3 cc. water and 0.375 gram of powdered permanganate, which are the same proportions as used in most of the experiments in Table II. The procedure was the same as described above.

TABLE VII.

Date	Formaldehyde found in bottle Per cent	Formaldehyde found in residue. Per cent.	Total found. Per cent.
I. 8/23, 1905.....	31.00	34.23	65.23
II. 8, 23, 1905.....	32.16	34.04	66.20

The percentage yield was about the same as that given in Table II, but less than that in the previous experiments (Table VI) with undiluted formalin. The formaldehyde remaining with the residue was about the same as in the previous experiments where powdered permanganate was used. The total formaldehyde found was less than in the experiments with undiluted formalin, indicating a greater destruction of formaldehyde.

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### THE AMOUNT OF SODIUM SULPHITE RECOVERABLE FROM FOOD PRODUCTS AS A BASIS FOR THE ESTIMATION OF THE AMOUNT ORIGINALLY PRESENT.

BY CLIFFORD D. HOLLEY.

Received April 4, 1906.

At a time when so many misleading statements are being made concerning sodium sulphite and sulphurous acid as food pre-

servatives and the amounts actually used in the preservation of meats and the bleaching of fruits, it is necessary in order to form an impartial judgment, to make a careful investigation of products actually offered for sale and especially those products which are used extensively. This paper embodies the results obtained by the writer in the Food Laboratory of the North Dakota Experiment Station.

Writers who advocate the use of preservatives would have us believe that sodium sulphite is always used in very small quantities. Dr. Calm, in his treatise on "Sulphurous Acid and Sulphites as Food Preservatives," when discussing the statement that sodium sulphite confers upon minced meat an abnormally brilliant red color, says, "this is not true of the very small amounts of sodium sulphite actually employed on meat, *e. g.*, 0.075 per cent." Again, further on in the same article he repeats this statement adding that 76 to 96 per cent. of this is oxidized to sulphate before the meat is eaten, and from the remaining per cent. of sulphurous acid, the amount naturally present in meat (0.0047-0.01 per cent.) must be deducted, the moiety of free sulphurous acid left in meat preserved by sulphites, is rather startling to those who claim that sodium sulphite as a food preservative is deleterious to health.

In order to determine the accuracy of these statements the following experiments were carried out. The sodium sulphite was added to freshly prepared pork sausage and determinations of the amounts recovered, calculated from the sulphurous acid distilled over, were made, after allowing the meat to stand for the various lengths of time.

TABLE I.—AMOUNTS OF SODIUM SULPHITE RECOVERED.

100 grams pork sausage mixed with 0.2 per cent. sodium sulphite	After 6 hours.	After 24 hours.	After 36 hours.	After 3 days.
I.....	49.75	32.43	23.06	23.28
II.....	26.15	30.85	25.10	22.81
III.....	33.15	31.75	24.16	22.11
IV.....	....	....	....	22.45
Average.....	36.35	31.68	24.11	22.66

Out of forty-three samples of pork sausage and Hamburg steak collected at different butcher shops throughout the state by

E. F. Ladd, Food Commissioner, thirty contained sulphites; of this number, eighteen were examined quantitatively and the following amounts of sodium sulphite, calculated from the sulphurous acid, were recovered. All of the samples were at least thirty-six hours old when analyzed and the majority of them were considerably older, as they had developed the odor of standing meat. Assuming from the above data that as much as one-fourth of the sodium sulphite was recovered, which is stating it very conservatively, the minimum per cent. originally present is given in the last column of the following table.

TABLE II.

100 grams of the samples were treated with phosphoric acid in the usual manner Lab No	Amount of sodium sulphite recovered Grams	Minimum. per cent. originally present.
2634, Pork Sausage.....	0 1315	0.53
2635, Sausage Meat.....	0 356	1.42
2636, Hamburg Steak .....	0 3515	1.41
2637, Sausage Meat .....	0 0294	0.37
2638, Hamburg Steak .....	0 131	0.52
2648, Sausage Meat.....	0 0494	0.20
2649, Sausage Meat .....	0.1206	0.48
2651, Sausage Meat .....	0 361	1.44
2652, Sausage Meat .....	0 0356	0.14
2681, Sausage Meat ...	0 0951	0.38
2683, Sausage Meat. ....	0 0931	0.37
2691, Sausage Meat .....	0 0894	0.36
2707, Sausage Meat .....	0 137	0.45
2708, Sausage Meat.....	0 054	0.22
2710, Sausage Meat.....	0.0758	0.30
2711, Sausage Meat.....	0.023	0.09
2734, Sausage Meat.....	0.044	0.18
2737, Sausage Meat.....	0.0385	0.15
Average.....	0.1265	0.50

In order to ascertain the amount recoverable when varying amounts of sodium sulphite were used with the same quantity of sausage, the following experiments were carried out. The meat stood four days after being treated with the sulphite. The distillates were collected in two portions.

TABLE III.

	Per cent first distillate 50 cc.	Per cent. second distillate 100 cc.	Total per cent. recovered.
100 grams meat used.			
I 0.2 gram sodium sulphite.....	16.94	6.07	23.01
II 0.3 gram sodium sulphite.....	11.81	6.90	18.71
III 0.4 gram sodium sulphite.....	18.98	3.56	22.54
IV 0.5 gram sodium sulphite.....	17.90	4.85	22.75
Average.....	16.41	5.35	21.75

Several portions of pork sausage were mixed with 0.2 per cent. of sodium sulphite and after standing twenty-four and thirty-six hours were fried in the usual manner and then distilled with phosphoric acid and the sodium sulphite calculated from the sulphurous acid, as usual.

TABLE IV.

Weight of meat, 100 grams.	After 24 hours.	After 36 hours.
I.....	27 72	20 81
II.....	27 08	20.70
III.....	28.22	20 28
Average.....	27.67	20.70

Table IV shows that very nearly as much sodium sulphite is recovered from the fried sausage as from that which has been subjected to the process of distillation only. It is very evident from a study of Table II that surprisingly large amounts of unoxidized sulphite are liable to be taken into the system. For example from laboratory numbers 2635, 2636 and 2651, 0.356 gram, 0.3515 gram and 0.361 gram of sodium sulphite were recovered from 100 grams of meat. Eighty grams of sausage would be easily eaten by an ordinary adult at a meal; this would mean about 0.3 gram of unoxidized sulphite taken into the system in the above instances, along with 1.0 gram, approximately, of sodium sulphate.

#### ESTIMATION OF COMBINED SULPHUROUS ACID IN DRIED AND EVAPORATED FRUITS.

Fourteen samples of dried or evaporated fruits offered for sale in this state were examined quantitatively for the amount of combined sulphurous acid present. The amount recovered, calculated as sodium sulphite, being given in the following table:

TABLE V.

Lab. No.	Amount of fruit used, 100 grams.	Amount recovered.
2604	Ruby Prunes.....	0.042
2607	Evaporated Apricots.....	0.165
2608	Evaporated Peaches.....	0.115
2617	Evaporated Peaches.....	0.112
2619	Ruby Prunes .....	0.190
2620	Dried Apricots. ....	0.149
2640	Silver Prunes .....	0.046
2653	Silver Prunes. ....	0.086
2666	Silver Prunes. ....	0.110
2685	Silver Prunes. ....	0.226
2730	Ruby Prunes. ....	0.141
2731	Ruby Prunes. ....	0.174
2732	Silver Prunes .....	0.123
2787	Ruby Prunes. ....	0.054

---

Average..... 0.124

The average amount of combined sulphurous acid calculated as sodium sulphite in the above analyses, approximates very closely that found in the preserved meats and is sufficient to condemn these fruits as an article of diet, when we consider that the amount recovered probably represents only a fraction of the amount originally present.

#### CONCLUSIONS.

(1) The amount of sulphites mixed with meats to preserve them is much larger than is generally supposed.

(2) The amount of sulphites recovered is approximately one-fourth the amount originally present.

(3) The amount of unoxidized sulphites in fried meats (sausage) is much larger than several writers would have us to believe.

(4) With dried fruits which have been bleached with sulphurous acid, free or combined, the amount remaining unoxidized in the fruit is large, averaging 0.124 per cent. in the above samples. In one instance as much as 0.226 per cent. was recovered, calculated as sodium sulphite.

# THE APPROXIMATE DETERMINATION OF COMMERCIAL GLUCOSE IN FRUIT PRODUCTS.

BY WILLIAM LYON.

Received June 21, 1906.

THE quantitative determination of commercial glucose in fruit products is of much importance in ascertaining their values commercially, as well as to the official chemist.

The method<sup>1</sup> adopted by the Association of Official Agricultural Chemists for the determination of commercial glucose requires, in addition to a polariscope, facilities which in a small laboratory quite frequently will be found lacking.

Since the soluble solids of fruits in most cases consist largely of sucrose and invert sugar, the approximate quantitative determination of commercial glucose in fruit products can be effected by calculating from the soluble solids and the invert polarization of a sample at the laboratory temperature.

The soluble solids are determined by calculating from the specific gravity of a solution of the product under examination, ascertaining from a table<sup>2</sup> the percentage by weight of solids corresponding to the specific gravity of the sample.

The normal weight of the sample (26.048 grams for the Schmidt and Haensch polariscope) is then clarified, inverted, cooled to the laboratory temperature, made up to 100 cc. and polarized in a 200 mm. tube.

Let  $a$  = Percentage of total solids.

$b$  = Polarization in sugar degrees, taken algebraically.

$x$  = Percentage of glucose.

$y$  = Percentage of sucrose and invert sugar.

Then after inversion, assuming that 1 per cent. of commercial glucose causes a rotation of  $+1.75^\circ$  and 1 per cent. of invert sugar a rotation of  $-0.34^\circ$ , at a temperature of  $20^\circ$ , we have:

$$X + y = a$$

$$\text{and } 1.75 x - 0.34 y = b$$

$$\text{Whence, } x = \frac{0.34 a + b}{2.09}$$

Thus a fruit juice containing 70 per cent. of total solids and polarizing  $+18^\circ$  after inversion contains approximately 20 per

<sup>1</sup> U. S. Dept. Agr., Div. Chem. Bull. 65, p. 48.

<sup>2</sup> Loc. cit. Table VI.

cent. of commercial glucose. Another fruit juice containing the same amount of solids and polarizing  $-5^{\circ}$  after inversion contains approximately 9 per cent. of glucose.

At  $22^{\circ}$  the formula becomes  $x = \frac{0.33}{2.08} \frac{a+b}{1}$ , and there is a decrease of one in the second decimal of both numbers for each rise of  $2^{\circ}$  in the temperature.

LOS ANGELES, CAL.

## AN IMPROVED CONDENSATION APPARATUS.

BY H. E. BARNARD AND H. E. BISHOP.

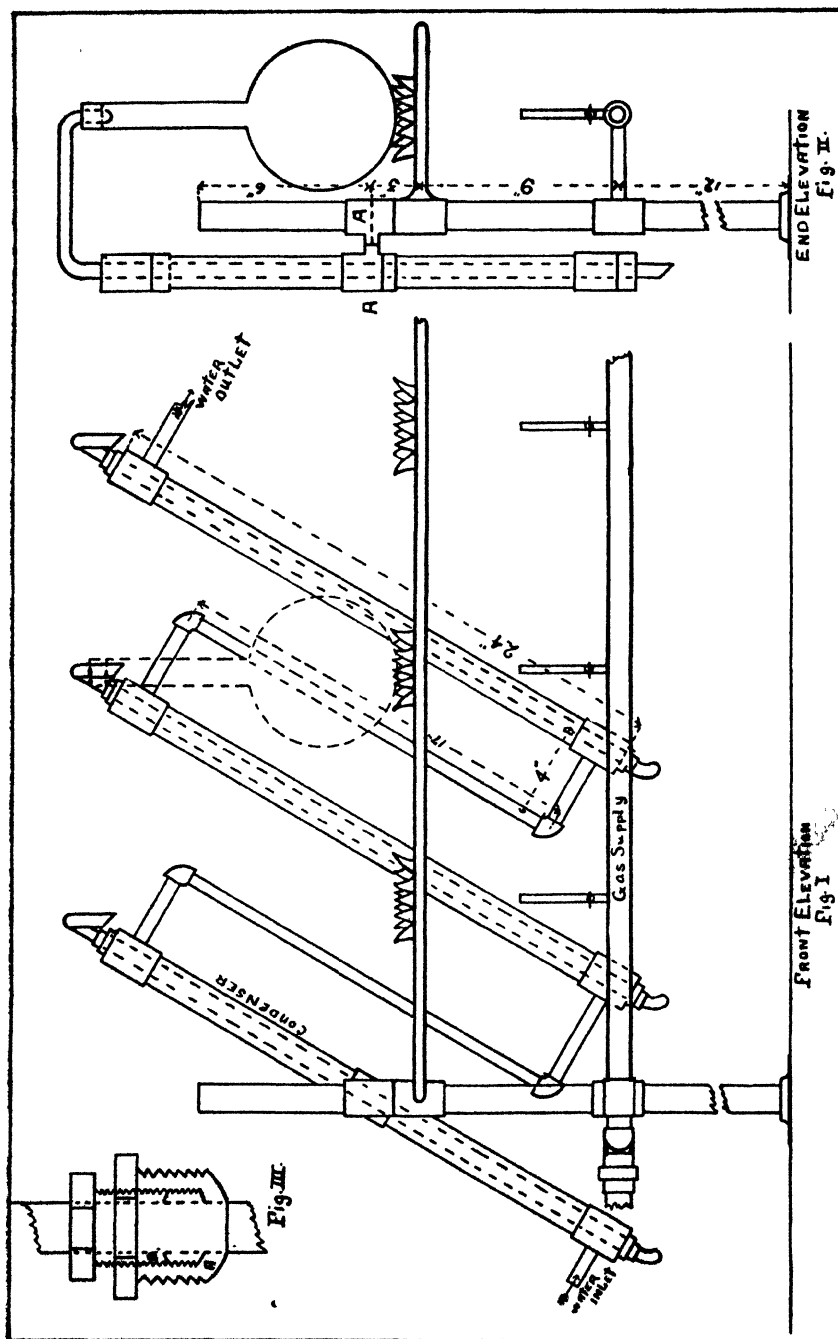
Received June 8, 1906.

FOR some years the earlier form of distillation apparatus, consisting of a copper tank through which the worm of the still passes, has been undergoing modifications and several very satisfactory types have been described which substitute for the condensation tank suitable piping so fitted that the worms pass through the pipe and are thereby constantly subjected to water under pressure.

We have recently designed and constructed a bank of stills, the arrangement of which is different from anything the writers have seen, and which is illustrated by the accompanying working drawings.

The apparatus consists essentially of three parts. The condensers, the support for the flasks and the battery of burners. For the condensers we use inch pipe for the water jackets, and three-eighths pipe for the connection from one jacket to the next. For the top and bottom of the water jacket, ordinary pipe fittings are used, one inch T's with a  $\frac{3}{8}$ -inch opening. To form a water-tight joint between the water jacket and the block-tin condensing tube, we use an ordinary packing box which is shown at Fig. III in the drawing. It is a brass cup, which fits into the end of the T, which in turn forms the end of the water jacket. B is the jam nut to press the packing against the block-tin tube shown in broken section. The tops of the cup and jam nut are made hexagonal so that they may be turned with a monkey wrench. By studying the drawing at Fig. II, A, it will be noticed that the water jackets are supported by placing a T in the centre of a water jacket tube. This is accomplished by using two short lengths of inch pipe instead of one long length as in the other water jackets.





This T is turned at an angle of  $90^\circ$  to the T's at either end of the water jacket; an ordinary  $\frac{3}{4}$ -inch plug screwed into the T and then a  $\frac{3}{4}$ -inch by  $\frac{3}{8}$ -inch cross screwed on to the plug. The threads are reamed out of the cross so that it will slip on the supporting tube easily. The other opening of the cross is filled with a plug with a set screw tapped into it to hold the water jackets in place. The support for the flasks is merely a gas pipe frame covered with galvanized iron. It is attached to  $\frac{3}{4}$ -inch by  $\frac{3}{8}$ -inch crosses to hold it in place, as are the water jackets. The openings for the flames are made by slitting the metal in the form of an asterisk (\*) and turning up the points in such a manner that they form a springy seat for the round-bottomed flasks. The gas supply pipe is attached to the supporting posts as are the water jackets and the flask support by  $\frac{3}{4}$ -inch by  $\frac{3}{8}$ -inch crosses with a plug containing a set screw in one side, and a  $\frac{3}{8}$ -inch nipple in the other side. The burners are attached to  $\frac{1}{8}$ -inch air cocks and these are tapped directly into the supply pipe. It will be necessary to rotate this pipe slightly when the burners are raised or lowered. Therefore the support for this pipe is made by reaming out the threads of a  $\frac{3}{4}$ -inch by  $\frac{3}{8}$ -inch T and allowing the gas pipe to slip through this T loosely. The connection with the gas supply will hold it in place. The ordinary Bunsen burner will just fit the  $\frac{1}{8}$ -inch thread on the air cocks so that no fitting is necessary here.

The posts supporting the apparatus are of  $\frac{3}{4}$ -inch pipe screwed into ordinary floor plates, which in turn are screwed to the table.

The appearance of the apparatus is greatly improved by a coat of aluminum bronze.

This apparatus possesses several advantages that makes it of value to chemists who have much routine work to do where distillations are required, as in water analysis, nitrogen determinations, alcohol estimations, etc. In the first place, a perfect condensation is always secured, as the water in the condensers is under ordinary hydrant pressure. We employ a gang of 10 stills and even when in constant use, the distillate is always perfectly cold. It takes up but little bench room because of the slanting arrangement of the condensers; the entire apparatus can be readily set up on a bench or shelf not over 12 inches deep, placed against the wall, and the distillates are always in easy reach. All parts are adjustable and any size flasks may be used by raising or lowering their support. The slant of the condenser makes it

possible by rotating the block-tin condensing tube to raise the distillation flask completely from its support. It may then be easily removed without danger of breaking. The apparatus costs but a third as much as when made with copper condensing tank, and is practically indestructible; the materials employed in its construction can be obtained of any plumber or gas fitter and put together with a pipe wrench. Under ordinary conditions the labor and material for a ten-tube still will not cost more than \$35.00.

STATE LABORATORY OF HYGIENE,  
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## SOME EXPERIMENTS ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COALS AND LIGNITES.<sup>1</sup>

BY E. E. SOMERMEIER.

Received May 28, 1906.

THE method in general use in this country for the determination of volatile combustible matter is that recommended by the Committee on Coal Analysis appointed by the American Chemical Society.<sup>2</sup> The directions given are as follows:

"Place 1 gram of fresh, undried, powdered coal in a platinum crucible, weighing 20 or 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear but the under surface should remain covered with carbon. To find 'Volatile Combustible Matter' subtract the per cent. of moisture from the loss found here."

This is the method used in the volatile determinations made in the Chemical Laboratory of the United States Geological Survey Fuel Testing Plant, the only modification being that the flame is protected from air currents by enclosing in a cylindrical

<sup>1</sup> Published by permission of the Director of the United States Geological Survey. Read before the Columbus Section of the American Chemical Society, May 23, 1906.

<sup>2</sup> This Journal, 21, 1122-1126.

asbestos shield 15 cm. long and 7 cm. in diameter, the platinum triangle being located 3 cm. below the top of the shield. The use of the shield gives more uniformity in the heat treatment with a corresponding greater uniformity of results. It is well recognized that variations in the size of the crucible, tightness of the lid, strength of the flame, etc., affect the process noticeably. Under uniform conditions the same operator usually has no great trouble with duplicates but it is quite probable that different operators working even under only slightly different conditions would have considerable trouble in duplicating results.

In most coals the routine results obtained in the laboratory have checked to within less than 0.3 or 0.4 per cent.; occasionally a sample has given trouble and the variation between duplicates without any apparent reason was as great as 1 per cent. On some lignites it has been found impossible to obtain close duplicates and on a few samples the carrying out of the official method gives very inaccurate results. This may be shown by the results obtained in the laboratory upon two different samples of the same lignite, which samples differed from one another only in the amount of moisture remaining in the air-dried sample and perhaps in the fineness of the grinding. The results on Sample No. 1 are as follows:

Moisture .....	9.88
Volatile matter .....	36.17
Fixed carbon.....	43.65
Ash ... ..	10.30
Sulphur.....	1.30

Sample No. 2.

Moisture .....	20.24
Volatile matter.....	58.48
Fixed carbon.....	10.85
Ash .....	10.43
Sulphur.....	1.03

This great difference in the fixed carbon results could not be accidental as all of the results on both samples were duplicated. A series of determinations was begun to determine, if possible, the cause of this great variation. Two causes were suspected and both were found to be partly responsible for the difference. (1) Mechanical loss due to the throwing out of solid particles by the too rapid expulsion of the volatile matter. The pos-

sibility of loss from this source is mentioned in the report of the committee but the results of their experiments are negative. (2) A different breaking down of the hydrocarbon compounds when expelled under different conditions and in the presence of variable amounts of moisture.

The results of Mr. N. M. Austin as published in the committee's report show that a preliminary treatment of the sample at a low heat and then the application of the full flame of the Bunsen burner gives higher results in fixed carbon than where the full flame of the Bunsen burner is applied from the beginning.

The proximate analysis of the sample of lignite giving the unusual results was finally reported by the laboratory as follows:

Moisture.....	20.24
Volatile matter.....	35.42
Fixed carbon.....	33.91
Ash.....	10.43
Sulphur.....	1.03

A series of seven results by the official method gave for volatile matter on this sample an average of 62.5 per cent. with a variation between high and low results of over 12 per cent. Three results of volatile matter on this sample made after previous expulsion of the moisture at 105° gave average volatile matter 39.6 per cent. with a variation between high and low results of 5.9 per cent. Preliminary treatment by driving off the moisture and most of the volatile matter at a low heat was then tried, the flame of the Bunsen burner being turned down to 10 cm. and the crucible gradually heated. The application of the heat was regulated by holding the burner in the hand and heating in such a way as to expel the moisture slowly and gradually smoke off most of the volatile matter, the volatile matter escaping freely enough during the last minute of this preliminary heating to burn with a small flame around the edge of the crucible cover. Two results with five minutes of preliminary heating and then seven minutes over the full flame of the Bunsen burner gave an average in volatile matter of 35.08 per cent., the variation between the two results being 0.23 per cent. Two results with three minutes' preliminary heating and seven minutes over the full flame of the Bunsen burner gave an average of 35.6 per cent. with a variation of 0.75 per cent. between results. A result

obtained by four minutes of preliminary heating and then seven minutes over the full flame gave 35.42 per cent. The difference in results obtained by the three, four and five minute preliminary treatment is small and in all subsequent experimental tests the time of the preliminary heating was four minutes. To determine the mechanical losses and difference in volatile compounds given off, a number of ash determinations were made after the driving off of the volatile matter by the official method and after driving off the volatile matter in connection with the preliminary heating. The results of volatile matter and ash on three determinations by the official method are as follows:

Volatile matter.....	66 72	67 47	54.82
Ash. . . . .	4 30	4 38	7.25 <sup>1</sup>

Two determinations with four minutes of preliminary heating and then seven minutes over the full flame gave:

Volatile matter.....	36.06	36.65
Ash. ....	11.16	11.15

That mechanical losses occurred during the rapid evolution of the volatile matter by the official method was also indicated by the shower of solid carbon particles driven off as sparks during the first few minutes, while with the preliminary heating these sparks were nearly or entirely absent. The average volatile matter on the first two determinations was 67.1 per cent., the average ash 4.34 per cent. The average volatile matter on the two results by the modified method was 36.35 per cent., ash 11.15 per cent. The moisture in the sample determined at this time was 19.78, giving fixed carbon 32.72 per cent. The difference in the ash results on the two pairs is 6.81 per cent., or the amount of sample driven off mechanically by the regular method is  $6.81 \div 11.15$ , or 61 per cent. Taking this portion of the fixed carbon result by the modified method gives 20 per cent. as the amount of fixed carbon expelled mechanically in the first determinations. The results on the official process after making this correction and also taking the correct ash value are as follows:

<sup>1</sup> This result is possibly explained by the fact that this sample stood for two hours in the crucible after weighing out and a considerable amount of the moisture content may have escaped before the sample was treated for the determination of the volatile matter.

Moisture.....	19.78
Volatile matter .....	47.10
Fixed carbon.....	21.97
Ash.....	11.15

---

100.00

After making this correction for mechanical losses the difference in the fixed carbon by the two processes is still 10.75 per cent., which difference must be due to the difference in the breaking down of the hydrocarbon compounds by the different heat treatment. The ash from the third result by the official method was 7.25 per cent. or the loss of ash 3.9 per cent. Correction for fixed carbon mechanically carried off is accordingly 3.9/11.15 or 11.4 per cent. The result, after making the fixed carbon and ash corrections, figures as follows:

Moisture.....	19.78
Volatile matter .....	43.42
Fixed carbon.....	25.65
Ash.....	11.15

---

100.00

The difference in this case in fixed carbon by the two methods due to the different heat treatment is 7.07 per cent.

*Effect of Fineness of Sample.*—This particular sample was very finely ground. To find out how much this difference in result was due to the fineness of grinding, a duplicate portion of the same sample was ground down till it passed a 40-mesh sieve. The results of duplicates by the official method and the modified method obtained are as follows:

	Official method.	Preliminary heating.
Volatile matter.....	42.07	35.72
Ash.....	10.25	11.20

Or loss in ash 0.95 per cent. The proximate analysis of the sample by the modified method is as follows:

Moisture.....	19.35
Volatile matter.....	35.72
Fixed carbon.....	33.73
Ash.....	11.20

---

100.00

The correction for fixed carbon to be applied to the result of the official method is 0.95/11.20 or 8.5 per cent. of the fixed

carbon result of the modified method, which is 2.9 per cent. The results by the official method after correcting for mechanical loss of fixed carbon and ash are as follows:

Moisture.....	19.35
Volatile matter.....	39.17
Fixed carbon.....	30.28
Ash.....	11.20

100.00

The difference in fixed carbon between the two methods due to different heat treatment is 3.45 per cent. These results show, at least, for lignites that the fineness of the sample has an important effect upon the result. Upon another sample of lignite similar to the one already tested, except that it contained more moisture (30.45 per cent.), the results obtained are as follows:

Average of results by the modified process:

Moisture.....	30.45
Volatile matter.....	30.97
Fixed carbon.....	27.75
Ash.....	10.83

100.00

The results in volatile matter and ash by the official method:

Volatile matter.....	44.40
Ash. . . . .	8.12

Hence, the correction to be applied to the fixed carbon and ash for mechanical loss is  $2.71/10.83$ . Applying these corrections, the results by the official method are:

Moisture. . . . .	30.45
Volatile matter.....	37.43
Fixed carbon....	21.29
Ash.....	10.83

100.00

The difference in the fixed carbon results between the two samples due to different heat treatment is 6.46 per cent.

To test the effect of the fineness of grinding upon the determination of the volatile matter in ordinary bituminous coal a sample of Kentucky coal containing 2 per cent. moisture, 5.7 per cent. ash and 0.9 per cent. sulphur was still further reduced in ash content by floating on a calcium chloride solution, sp. gr.



1.32. The lighter portion was then thoroughly air-dried and separated by sifting into the following sizes:  $1/4$  to  $1/10$ ,  $1/10$  to  $1/20$ ,  $1/20$  to  $1/40$ ,  $1/40$  to  $1/80$  and  $1/80$  and finer. The proximate analyses of the samples by the official method are as follows:

	Moisture.	Volatile matter.	Fixed carbon.	Ash.
$1/4-1/10$ .....	1.15	39.05	58.20	1.60
$1/10-1/20$ .....	1.45	38.80	58.55	1.20
$1/20-1/40$ .....	1.70	38.55	58.35	1.40
$1/40-1/80$ .....	1.90	38.05	58.40	1.65
$1/80$ and finer.....	2.05	35.54	59.66	2.75

By the modified process with four minutes of preliminary heating the result in volatile matter on the  $1/20$  to  $1/40$  size was 33.75 per cent. and on the  $1/80$  and finer 32.85 per cent.

The results in volatile matter on these different sizes are somewhat higher on the coarse samples. However, the different ash contents of the different sizes indicate that the sizing had to a degree separated the coal into somewhat different varieties, as the higher ash content of the finer sample would not in itself be sufficient to account for the lower volatile results. In order to see whether the difference was due to the fineness of grinding or difference in the coals, a portion of the  $1/20-1/40$  sample was ground down in an agate mortar and the volatile matter determined on this fine portion. The average of several results was 37.6 per cent. as against 38.55 per cent. on the coarse sample.

From this series of results it appears, at least in low moisture bituminous coals, that the finer ground samples give somewhat lower volatile matter than the coarser samples, probably due to the more complete sintering together of the fine samples upon heating, with the consequent effect upon the giving off of the volatile matter.

*Effect of Different Heat Treatment.*—In order to find out how much effect different heat treatment has on different coals, a series of samples was selected ranging from anthracite to peat, most of the samples used in the tests having been previously more or less completely air-dried so as to permit of better handling in the laboratory. Determinations for volatile matter were made in duplicate by the regular official method and by the four-minute preliminary heating method. The proximate analysis of the samples with the volatile matter determined by the official method is tabulated in the first five columns; the results for volatile matter by the preliminary heating are given in the sixth column; the

differences in volatile matter by the two methods are given in the seventh column. The determinations for moisture were all made in accordance with the official method by weighing out a separate sample. The same is true of the determinations for ash with the exception that upon two or three of the lignite samples and one of the Pennsylvania samples the results for ash are those obtained after the determination of the volatile matter by the modified process. These particular samples and results are all specifically mentioned elsewhere in this paper.

Source of coal.	Moisture.	Official method. Volatile matter.	Fixed carbon.	Ash	Sulphur	Volatile matter with four min- utes' preliminary heating.	Difference.
Colorado anthracite..	2 80	5 05	77 55	14 60	0 60	4.90	0.15
Arkansas . . .	0.83	12 47	72 05	14.65	2.14	12.37	0.10
Pennsylvania.....	0.90	17.35	74 92	6.83	0.97	16.07	1.28
Pennsylvania.....	1 05	33.10	53.30	12 55	1.76	30.35	2.75
Kentucky... ..	2 99	37 51	56.68	2 82	0.58	34.78	2 73
Indiana... ..	4 20	37 70	45 65	12 45	4.13	34 67	3.03
Washington . . . . .	6 65	35 87	44 57	12 91	0.68	34.25	1.62
Indiana. . . . .	8 40	34 40	48 72	8 48	1 47	32.00	2.40
North Dakota (lignite). . . . .	11 65	45 58	32 97	9.80	1.04	40 17	5.41
Illinois. . . . .	12 40	32.18	42 82	12 60	1.30	30.12	2.06
Texas lignite (fine) ..	19 78	62.50	6 57	11 15	1.03	35 42 <sup>1</sup>	27.08
Texas lignite (40- mesh duplicate. . .	19 35	42 07	27 38	11 20	.	35 72	6.35
Texas lignite (not air-dried).....	30.45	44 40	15 42	9 73	....	30.97	13.43
Massachusetts peat ..	13 25	49 80	16 21	20 74	0.58	47.92	1.88

With the exception of the anthracite and semi-anthracite samples, the results by the preliminary heating as compared with the official method all show a considerably less amount of volatile matter and a correspondingly greater amount of fixed carbon. In the case of the lignites, the greater volatile matter by the official method, as has been shown, is partly due to mechanical losses.

<sup>1</sup> Two determinations upon the fine sample of Texas lignite made by heating for four minutes over a flame 5 cm. high and then seven minutes over the full flame (25 cm.) gave 35.47 per cent. volatile matter. Almost an exact check upon the result obtained by the four-minute preliminary heating with a 10 cm. flame regulated by holding burner in the hand.

In order to see if mechanical losses might account for the differences on the bituminous coals, determinations for the ash after the determination of the volatile matter were made on one of the Pennsylvania samples. The average results for ash on the samples by the two methods are as follows:

	Ash.
Official method.....	12 56
Preliminary heating.....	12.53

These results indicate no mechanical loss whatever and in none of the samples except the lignites were visible solid carbon particles driven off in the form of sparks, and the differences must be ascribed to the different breaking down of the hydrocarbon compounds by the difference in heat treatment.

*Effect of the Presence of Moisture.*—Comparisons of the results of volatile matter on a great number of samples differing from one another in moisture content indicate that the presence of loosely held moisture in the sample causes a higher volatile result. In order to obtain more definite data on this question three samples low in moisture and representing widely different kinds of coal were selected for a series of determinations. The effect of loosely held moisture upon the determinations for volatile matter in each of these samples was determined by adding to the sample after weighing out definite amounts of water, which was thoroughly mixed with the sample by means of a fine platinum wire and the volatile determination then made in the usual manner according to the official method. The first sample selected was a sample of Pennsylvania coal. The proximate analysis of the air-dried sample is as follows:

Moisture.....	1.05
Volatile matter...	33.00
Fixed carbon.....	53.30
Ash.....	12.55
Sulphur.....	1.75

The results for volatile matter in this sample determined in the presence of additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture.....	33.60
With 0.1 gram additional moisture.....	33.70
With 0.15 gram additional moisture.....	33.80
With 0.2 gram additional moisture.....	34.10
With 0.3 gram additional moisture.....	33.90

The second sample was an air-dried sample of Illinois coal, the proximate analysis of which by the regular official method is as follows:

Moisture.....	2.35
Volatile matter.....	39.35
Fixed carbon.....	44.65
Ash.....	13.65

The results of volatile matter with the additional moisture added to the sample are as follows:

	Volatile matter.
With 0.03 gram additional moisture.....	39.60
With 0.05 gram additional moisture. ....	39.30
With 0.10 gram additional moisture.....	40.00
With 0.15 gram additional moisture. ....	40.05
With 0.2 gram additional moisture.....	39.75

The third sample was an air-dried sample of Arkansas lignite, the proximate analysis of which by the official method is as follows:

Moisture....	10.85
Volatile matter. .	38 50
Fixed carbon..	31.40
Ash.....	19.25
Sulphur.....	0.83

The results for volatile matter with the additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture.....	40.35
With 0.10 gram additional moisture.....	41.20
With 0.15 gram additional moisture.....	40.90
With 0.20 gram additional moisture.....	44.90

Without exception all of these results show that the presence of loosely held moisture in the sample increases the value obtained for the volatile combustible matter. The average increase for the Pennsylvania sample is about 0.7 per cent. On the Illinois sample the increase for volatile matter is 0.4 per cent. On the Arkansas lignite the increase is 3.3 per cent.

To see what effect this loosely held moisture might have on the volatile determinations where the sample was first subjected to four minutes of preliminary heating over a low flame determinations were made upon these samples with and without additional moisture. The results are as follows:

Pennsylvania sample with no moisture added, volatile matter 30.35. With 0.3 gram added, the volatile matter 31.65.

The Illinois sample with no moisture added, volatile matter 34.85. With 0.15 gram moisture added, volatile matter 36.10.

The lignite sample with no moisture added, volatile matter 36.90. With 0.2 gram moisture added, 37.40.

These results show that even with a gradual preliminary heating the presence of loosely held moisture increases the value of the volatile determinations, the difference in some of the samples being as great as the difference by the official method, from which it appears that the rapid application of heat sufficient to drive off this moisture results in a reaction between the water vapor and the carbon or hydrocarbons in the coal.

*Conclusions.*—The results of the foregoing experiments and tests show that the value obtained for volatile matter in coal is affected to an important degree by the method of heating the sample, by the fineness of pulverization and by the amount of loosely held moisture present. In bituminous coals these differences do not exceed 3 or 4 per cent. and appear to be entirely due to a different breaking up of the hydrocarbon compounds under the different conditions of heat treatment, fineness of sample and amount of moisture present. In the case of lignites where the difference may be as high as 25 per cent. this difference is largely due to the mechanical loss in the sample during the rapid expulsion of the volatile matter.

*Correctness of Results.*—Since the determination of the volatile matter is a purely arbitrary one unless mechanical loss can be shown, as in the case of lignites, it appears that any results obtained by following out the regulation method should be considered as correct, any difference in results due to differences in fineness of pulverization or to the amount of moisture present having no effect upon the correctness of the value actually obtained. The differences due to difference in pulverization or moisture content do, however, have a very important effect when it comes to the question of different chemists obtaining concordant results upon different samples of the same coal.

In regard to the difference in results obtained due to a different heat treatment, while the method of heating as given by the official method may be considered as giving the correct result it does not necessarily give us a result approximating very closely

the volatile matter as given off when the coal is fired under a steam boiler or especially when coked in a coke oven, as under these conditions the volatile matter is driven off gradually and during a considerable interval of time, and it appears that the slower driving off of the volatile matter from the sample in the laboratory gives results more in accordance with these conditions than does the official method. This latter fact is, however, a matter of minor importance, for so long as all volatile determinations are done in the same way it makes very little difference what that way is.

In the case of lignites where the application of the official method causes mechanical losses it appears desirable and necessary that the committee so modify the official method for volatile matter in lignites as to prevent this loss, and the results of these foregoing determinations and experiments are published at this time with a view of bringing this matter before the committee and the public.

U S GEOLOGICAL SURVEY,  
FUEL TESTING LABORATORY

## THE RELATION OF SODIUM TO POTASSIUM IN SOIL AND SOLUTION CULTURES.<sup>1</sup>

BY J F BREAZEALE

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THE determination of the exact amount of salt absorbed from solution by plants during the process of growth has been the subject of many experiments in former years. The ordinary gravimetric or volumetric methods which have usually been employed in such investigations have been on the whole inadequate for such work. The soil solution or the nutrient solution best suited to the requirements of most plants is usually of such a low total salt content that slight changes in its concentration cannot be detected by ordinary analytical means without the expenditure of an amount of time which is almost prohibitive. In the same way the amount of salt a seedling will absorb from solution in the course of a short period of its growth is usually too small to be detected by such methods.

For several years past the Bureau of Soils has been devising and adapting analytical methods which are well suited to such

<sup>1</sup> Published by permission of the Secretary of Agriculture.

investigations.<sup>1</sup> These methods have opened up a comparatively new field for experimental work with the soil and soil solutions and offer a ready means of attacking some of the hitherto difficult problems of plant nutrition.

During the spring and summer of 1905 while engaged in the study of certain soil problems in coöperation with the Rhode Island Experiment Station an opportunity was offered of carrying on, with water and soil cultures, the experiments which are here reported.

The direct object of these experiments was to bring to bear upon the plot work, on the replacement of potassium by sodium, which is being conducted at the Rhode Island Station, the delicate analytical methods as well as the pot and water culture methods used by the Bureau of Soils.<sup>2</sup>

The nature of the plants which had best responded to the application of sodium salts in the field—beets, radishes, turnips, etc.—made it almost impossible to use them in such work; so wheat was selected, as it offered few difficulties in the way of sprouting and handling. The seeds were sprouted on a piece of mosquito netting stretched over a shallow basin of distilled water and kept moist by contact with its surface. When the plumules had reached a length of about 5 cm. the seedlings were transferred to bottles containing the nutrient solutions. The seeds were removed from the seedlings before beginning the experiment, and all further supply of nutrient materials from this source was thus eliminated. With the exception of the first experiment the bottles containing the nutrient solutions were of dark brown glass and held 600 cc. each. "Chemically pure" salts were used to make up these solutions. They were accurately standardized in strengths of 1/5 normal and then diluted to the desired concentrations. The water used in these experiments was shaken up with carbon black and filtered through a Pasteur-Chamberland filter before using.<sup>3</sup> The work was carried on in

<sup>1</sup> "Colorimetric, Turbidity and Titration Methods used in Soil Investigations," Bull. 31, Bureau of Soils, U. S. Dept. of Agric., 1906.

<sup>2</sup> See Annual Reports and Bulletins 104 and 106 of the Rhode Island Experiment Station.

<sup>3</sup> On the beneficial effects of this treatment upon distilled water see Breazeale, J. F.: "Effect of Certain Solids upon the Growth of Wheat in Water Cultures," *Bott. Gazz.* 41, 54 (1906).

a greenhouse and the solutions containing the cultures were changed every four days.

After much preliminary work, a series of six nutrient solutions was prepared, having the following salt content in parts per million:

TABLE I.  
Parts per million.

1.	2.	3.
CaCl <sub>2</sub> ..... 44	NaCl..... 44	CaCl <sub>2</sub> ..... 44
MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24
Na <sub>2</sub> HPO <sub>4</sub> ..... 38	Na <sub>2</sub> HPO <sub>4</sub> ..... 38	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ... 38
KNO <sub>3</sub> ..... 80	KNO <sub>3</sub> ..... 80	Ca(NO <sub>3</sub> ) <sub>2</sub> ..... 80
FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12
Total .....198	198	198
4.	5.	6.
CaCl <sub>2</sub> ..... 44	CaCl <sub>2</sub> ..... 44	CaCl <sub>2</sub> ..... 44
MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24
(Na) <sub>2</sub> HPO <sub>4</sub> ..... 38	K <sub>2</sub> SO <sub>4</sub> ..... 38	K <sub>2</sub> SO <sub>4</sub> ..... 38
NaNO <sub>3</sub> ..... 80	NaNO <sub>3</sub> ..... 80	(Na) <sub>2</sub> HPO <sub>4</sub> ..... 80
FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12
Total .....198	198	198

It has already been shown that the concentration of the nutrient solution has an important effect upon water cultures,<sup>1</sup> so care was taken to have each of these solutions of the same total salt content and of a concentration well suited to the growth of wheat. Solution No. 1 was a full nutrient solution, *i. e.*, a solution containing all of the bases and acids usually classified as plant foods. No. 2 contained all of these nutrients except calcium, this element being replaced by sodium. In No. 3 both sodium and potassium were left out and ammonium and calcium substituted. In No. 4 potassium alone was omitted and sodium substituted. In No. 5 PO<sub>4</sub> was replaced by SO<sub>4</sub>, and in No. 6 NO<sub>3</sub> was replaced by SO<sub>4</sub>. It will be noticed that in making these substitutions acids or bases were used which are known to have but little effect upon the plant. They were added for the sole purpose of bringing up the total salt content.

¶ Sixteen wheat seedlings were placed in 240 cc. of each of these solutions in the manner described in Bulletin No. 23 of the Bureau of Soils and allowed to grow for fifteen days. The solutions were

<sup>1</sup> Breazeale, J. F.: Science, N. S. 22, 146 (1905), "Effect of the Concentration of the Nutrient Solutions upon Wheat Cultures."



frequently changed so that an abundance of plant food was always present. At the end of this period the plants were taken from the solutions in which they had been growing and each set placed in 240 cc. of a full nutrient solution having the following concentration of nutrients by analysis:

	Parts per million
Ca (calcium).....	27.2
K (potassium) .. .	42.0
PO <sub>4</sub> (phosphates).....	51.7
NO <sub>3</sub> (nitrates).....	68.8

The salts used in this nutrient solution were the same as those in No. 1 but the amounts were increased slightly in order to have enough left for an analysis after the plants had grown in the solution for the period during which they were under observation. The bottles containing the cultures were then weighed and allowed to stand for two days. At the end of that time they were again weighed, the difference in weight representing the amount of water lost by transpiration. The solutions were then made up to their original volume with distilled water and analyzed for calcium, potassium, phosphates and nitrates.

Table II represents the transpiration of the plants in grams and the amounts, in parts per million, of the nutrients removed from the above-mentioned solution.

TABLE II.

Solution in which seedlings grew during first period.	Transpiration of seedlings and the parts per million of nutrients removed from the full nutrient solution during the second period.				
	Trans.	NO <sub>3</sub>	Ca.	K	PO <sub>4</sub> .
1. Full nutrient.....	65	40.4	4.0	9.0	9.4
2. Nutrient with Ca left out.....	47	42.1	6.4	9.0	4.7
3. Nutrient with both K and Na left out.....	20	10.7	4.0	15.0	0.7
4. Nutrient with K left out .....	64 <sup>1</sup>	53.8	4.8	36.0	6.6
5. Nutrient with PO <sub>4</sub> left out.....	26	25.8	4.8	6.0	6.6
6. Nutrient with NO <sub>3</sub> left out .. .	29	60.2	3.2	12.0	0.7

The general development of the plants in this experiment was in the same relative order as their transpirations.<sup>2</sup> As indicated by the transpiration figures, the plants in No. 1 were

<sup>1</sup> Owing to an oversight the seeds were not removed from the seedlings of No. 4 until one day after the experiment was begun. This accounts for the relatively high transpiration.

<sup>2</sup> For evidence in regard to the use of transpiration as a criterion here, see Livingston, B. E.: "Relation of Transpiration to the Growth of Wheat," Bot. Gaz. 40, 178 (1905).

more than three times as large as those in No. 3; the proper basis of comparison therefore should be the relative size of the plants. In the absence of the absolute weight of the plants, the data for such a comparison may be obtained by dividing the total amount of the different nutrient constituents taken out of solution by the amount of water transpired by the plants. The following table represents in parts per million the amount of calcium, potassium, phosphates and nitrates removed from the original solution for every 10 grams of water transpired by the plants. Since 240 cc. of water were used, one part per million in the table is equivalent to 24 mg.

TABLE III.

Solution in which seedlings grew during <i>first</i> period.	Parts per million of nutrients removed from the nutrient solution during <i>second</i> period for every 10 grams of water transpired by seedlings.			
	NO <sub>3</sub>	Ca.	K.	PO <sub>4</sub> .
1. Full nutrient . . . . .	6.21	0.61	1.38	1.45
2. Nutrient with Ca left out....	8.95	1.36	1.92	1.00
3. Nutrient with K and Na left out .....	5.35	2.00	7.50	0.35
4. Nutrient with K left out....	8.40	0.75	5.62	1.03
5. Nutrient with PO <sub>4</sub> left out...	9.92	1.85	2.30	2.54
6. Nutrient with NO <sub>3</sub> left out...	20 76	1.10	4.14	0.24

Using as a basis of comparison the full nutrient solution No. 1, it will be noticed both from Table II and from Table III that in the case of the plants which had been grown for the first fifteen days of their life in a solution from which had been omitted either nitrates, phosphates or potash, these plants, when placed in a full nutrient solution, took up relatively a much larger amount of that particular nutrient which had been left out of the first solution. This is probably also true in the case of calcium, as is indicated in Table II, but is not apparent when calculated on the basis of equivalent plant development as is shown in Table III. For example, No. 6 in Table III, which had been previously grown without nitrates, the seedlings when placed in a solution containing that nutrient took up more than twice as much nitrates as did any of the others. From these results it is apparent that in the manner just described a demand for either of the three most important constituents of mineral plant food, nitrates, phosphates, or potash can be created within the plant and that this demand can be measured by analytical methods.

As indicated in both the preliminary work and in the experi-

ment just described, plants which for the first period grew in a solution containing sodium but no potassium drew less heavily upon the potassium of the full nutrient solution than the plants which for the first period grew in a solution containing neither sodium nor potassium. There was a greater absorption of potassium where sodium had been absent than where it had been present. This seemed to indicate that sodium was in some way affecting the absorption of potassium, and to investigate this question the following experiments were carried out.

Four nutrient solutions were prepared having the following salt content in parts per million:

TABLE IV.

1.	2.	3.	4.
CaCl <sub>2</sub> ..... 44	CaCl <sub>2</sub> ..... 44	CaCl <sub>2</sub> ..... 44	CaCl <sub>2</sub> ..... 44
MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24	MgSO <sub>4</sub> ..... 24
Na <sub>2</sub> HPO <sub>4</sub> ... 38	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 38	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 38	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 38
KNO <sub>3</sub> ..... 80	KNO <sub>3</sub> ..... 80	NaNO <sub>3</sub> ..... 80	Ca(NO <sub>3</sub> ) <sub>2</sub> .... 80
FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12	FeCl <sub>3</sub> ..... 12
Total ..... 198	198	198	198

No. 1 was a full nutrient solution, No. 2 a solution with sodium omitted, No. 3 with potassium omitted, and No. 4 with both sodium and potassium omitted. Eight wheat seedlings were placed in 600 cc. of each of these solutions and allowed to grow for nineteen days with frequent changes of solution. The plants showed marked differences from the first as is shown by the following transpirations.

TABLE V.

No.	Solution.	Transpiration Grams
1.	Full nutrient.....	130
2.	Nutrient without sodium.....	112
3.	Nutrient without potassium .....	89
4.	Nutrient without both sodium and potassium ...	86

After nineteen days the cultures were taken from these solutions and each placed in 600 cc. of a full nutrient solution containing 18.3 parts per million of potassium and allowed to grow for one day. The losses by transpiration were determined, the solutions made up to their original volumes and analyzed for potassium.

Table VI represents the transpiration of the plants, parts per million of potassium removed from solution, and parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VI.

Results for the second period.

Solution in which seedlings grew during first period.	Trans- piration. Grams	Potassium removed from the nutrient solution.		
		On the basis of 10 grams of water transpired.		
		P p.m.	P p.m.	Mgs
1. Full nutrient solution.....	39.5	8.16	2.06	1.24
2. Nutrient without sodium.....	36.	15.71	4.36	2.61
3. Nutrient without potassium...	26.	12 65	4.86	2.92
4. Nutrient without both sodium and potassium.....	21 1	16.12	7.63	4.58

The plants were then mounted and photographed and are shown in Fig. 1.

It will be seen from the figure and by a comparison of the transpiration results of Nos. 1 and 2 that the presence of sodium has increased the transpiration and size of the plants, and this even where there was an abundance of potassium and all the other necessary mineral plant food constituents in solution. Apparently, a direct need for sodium was manifested by the plants in this experiment. This difference in transpiration and size appeared throughout all subsequent work but is seldom noticed when the seeds are not removed from the seedlings before beginning the experiment. It thus seems that the amount of sodium required by the plants during this period of their growth is small.

The difference in transpiration of Nos. 3 and 4 is much larger than appeared in subsequent work, and indeed somewhat larger than the general appearance of the plants would indicate. As a general rule the effect of sodium in increasing the size of the plant is not marked where there is no potassium present as is clearly shown in the experiments to follow.

It will also be noticed from the table that the phenomenon indicated in the first experiment is brought out more strikingly here. There was a greater demand for potassium in the plants growing in solution No. 2 where sodium was left out during the first period than in those of solution No. 1, which had always had an abundant supply of sodium.

In the following experiment the same number of seedlings were grown for fifteen days in solutions prepared in exactly the same way as those of the preceding experiment. At the end of that time the plants were removed from these solutions and all placed

in a full nutrient solution containing 36.4 parts per million of potassium and allowed to grow for two days. The loss by transpiration was then determined, the solutions made up to their original volumes and analyzed for potassium. Table VII represents the transpiration for two days, the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VII.

Solution in which seedlings grew during first period.	Trans- piration. Grams.	Results for the second period		
		Potassium removed from the nutrient solution.		
		On the basis of 10 grams of water transpired.		
		P p m.	P.p m	Mgs.
1. Full nutrient solution.....	15.8	1.04	0.65	0.39
2. Nutrient without sodium.....	11.0	6.24	5.67	3.40
3. Nutrient without potassium.....	6.1	5.20	8.52	5.11
4. Nutrient without sodium and potassium .....	7.8	6.24	8.00	4.80

Here also the comparison of the transpiration figures for Nos. 1 and 2 shows the beneficial effects of sodium upon the plants in the presence of an abundance of potassium. In the case of Nos. 3 and 4, however, this effect is not shown.

As in the previous experiment, the measured demand for potassium is much greater in No. 2 than in No. 1, but not so great as in No. 3, as shown in the third column of the table. This indicates that in water cultures the wheat plant does not absorb as much potassium, even when an abundance of that element alone is present, as it does when an adequate supply of sodium is also present.

Whether the ammonium salt which was substituted in Nos. 2, 3 and 4 played any part in the absorption of potassium was a point that was next considered. Four nutrient solutions were prepared in the manner indicated in Table VIII.

TABLE VIII.

	Parts per million.						
	CaCl <sub>2</sub> .	MgSO <sub>4</sub> .	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .	FeCl <sub>3</sub> .	KNO <sub>3</sub> .	NaNO <sub>3</sub> .	NH <sub>4</sub> NO <sub>3</sub> .
1 .....	44	24	38	12	40	40	0
2 .....	44	24	38	12	80	0	0
3 .....	44	24	38	12	0	80	0
4 .....	44	24	38	12	0	0	80

Twelve seedlings were placed in 600 cc. of each of these solutions and allowed to grow for seven days. The transpirations for the last day were as follows:

No.	Transpiration. Grams.
1.....	8.0
2.....	6.5
3.....	4.0
4.....	3.5

The plants were then removed from these solutions and placed in a full nutrient solution containing 73.9 parts per million of potassium, and allowed to grow for four days. The transpirations were then taken, the solutions made up to their original volumes and the amounts of potassium remaining in solution determined. In Table IX will be seen the transpiration of the plants in grams; the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE IX.

Results for the second period.

Solution in which seedlings grew during first period.	Trans- piration Grams	Potassium removed from the nutrient solution.		
		On the basis of 10 grams of water transpired.		
		P. p m	P p m.	Mgs.
1. Full nutrient solution.....	53.6	12.3	2.3	1.38
2. Nutrient without sodium.....	46.7	18.5	4.0	2.40
3. Nutrient without potassium...	33.5	16.2	4.8	2.88
4. Nutrient without sodium and potassium.....	34.7	23.0	6.6	3.96

These results are in harmony with those obtained in the earlier experiments.

The results obtained by keeping the plants in solutions in the first period were of such interest that it seemed desirable to ascertain what results would follow if the plants were kept during the first period in the soil itself. To this end about 500 grams of soil were taken from each of three plots of the Rhode Island Experiment Station. These plots are in what is known as the "soda-potash experiment," and have been under observation for the past ten years.<sup>1</sup> Their numbers are given below. They have all received equal yearly applications of nitrogen and phosphates in some combination, with varying amounts of either

<sup>1</sup> See Annual Reports of the Rhode Island Experiment Station.

potassium chloride or of sodium chloride, or both of these salts, excepting in the years 1902-1904, inclusive. The samples taken were given applications of ammonium nitrate and ammonium phosphate at the rate of 350 and 150 pounds per acre respectively, this being about the rate of application for nitrates and phosphates used in the field on these plots in 1905. Potassium chloride and sodium chloride were then added in the amounts indicated in Table X. This soil had been limed twice and was in good physical condition. The soil was then placed in small paraffined wire pots of the form described in Bulletin 23 of the Bureau of Soils, and eight radish seeds planted in each. The soil was kept at the optimum moisture content and the plants allowed to grow for thirty-two days.

The difference in size of the plants can be seen from Fig. 2, the numbers in the photograph corresponding to the plot numbers.

The plants were then carefully taken from the soil, their roots washed clean, and transferred to bottles of a full nutrient solution containing 61.6 parts per million of potassium and allowed to grow for three days longer. They were then taken from the solution and weighed. The solutions were made up to their original volume and analyzed for potassium. Table X represents the plot numbers, applications of potassium chloride and sodium chloride to the soil, green weight of crop, and parts per million of potassium subsequently removed from the nutrient solution for every gram of crop.

TABLE X.

Plot No.	Amount of potassium chloride and sodium chloride added to soil.	Green weight. Grams	P. p. m. of potassium removed for every gram of green weight.
16.	No potassium chloride, 200 lbs. per acre of sodium chloride...	4.4	5.9
22.	362 lbs. per acre of potassium chloride. No sodium chloride	6.0	4.1
17.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	11.65	2.5

Plot 16 had not received any potassium for a period of ten years, and this is distinctly shown by the relatively low weight of the crop. The increase in weight of No. 17 over No. 22 is the result of the application of sodium.

Here again as in the solution cultures there was a greater demand for potassium in the plants which had been growing in a soil which had received no potassium than in the plants which had always had a sufficient quantity of that element. There was also a greater absorption of potassium in No. 22 than in No. 17, although in the soil each had the same supply of that element. This indicates, as in the solution cultures, that sodium plays some part in the absorption of potassium. This experiment was repeated as Experiment VI.

The following experiment was similar to the preceding one excepting that soil from plots 4, 10 and 5 was used in this case. These plots corresponded in treatment to plots 16, 22 and 17, respectively, with the exception that plots 4, 10 and 5 had been limed only once. Sixteen radish plants were grown in pots of these soils for twenty-four days. The difference in growth is fairly represented by the following transpirations for one day at the end of that period.

Plot No.	Transpiration in grams.
4	72.
10	105.5
5	120.0

Four plants were selected from each of these plots, placed in a full nutrient solution containing 56.4 parts per million of potassium and allowed to grow for six days. Table XI represents the treatment of the soil, green weight of the plants used, and the parts per million of potassium removed from solution for every gram of green weight.

TABLE XI.

Plot. No.	Amounts of potassium chloride or sodium chloride added.	Green weight. Grams.	P. p. m. of potassium removed for every gram of green weight.
4.	No potassium chloride. 200 lbs. per acre of sodium chloride.....	3.50	7.54
10.	362 lbs. per acre of potassium chloride. No sodium chloride...	2.35	5.10
5.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	4.44	2.97

As the total weight of the crop is not of interest in this connection, plants were selected which were best suited for solution culture. This accounts for the high weight of the four plants selected in No. 4, the average plant in No. 4 being smaller than in



either of the other two. Here again the need of potassium in the plants of No. 4 is strikingly shown by the relatively large amount of that element which they removed from the nutrient solution. The effect of sodium upon the absorption of potassium is also brought out here.

The experiments just described were performed in the spring and summer of 1905. The plots in the "soda-potash" experiment of the Rhode Island Experiment Station were then in turnips and radishes. These were harvested about the middle of August and the plots planted in beets as a second crop. The plots received at the beginning of the season the full application of fertilizers for the year, *viz.*, 1,000 pounds of dried bone, 20 pounds of magnesium sulphate, and 1,500 pounds of dissolved bone. The quantities of potassium and sodium salts when applied to the plots under consideration here were 362 pounds of potassium chloride, and 200 pounds of sodium chloride per acre. No fertilizers were applied when the beets were planted. When the beets were about two weeks old, four plants were taken from each of the plots before mentioned, their roots washed clean, and placed in 100 cc. of a full nutrient solution containing 43.1 parts per million of potassium and allowed to grow for three days. They were then withdrawn and weighed, the solutions made up to their original volumes and analyzed for potassium.

Table XII represents the applications of potassium chloride and sodium chloride, green weight of plants, and parts per million of potassium removed from solution for every 1 gram of green weight.

TABLE XII.

Plot No.	Applications of potassium chloride and sodium chloride				Green weight. Grams.	P. p. m. of potassium removed from solution for every gram of green weight.
4.	0 pounds per acre KCl					
	200	"	"	NaCl	4.20	1.83
10.	362	"	"	KCl		
	0	"	"	NaCl	8.55	1.08
5.	362	"	"	KCl		
	200	"	"	NaCl	9.05	0.85
16.	0	"	"	KCl		
	200	"	"	NaCl	5.50	4.48
22.	362	"	"	KCl		
	0	"	"	NaCl	8.00	1.15
17.	362	"	"	KCl		
	200	"	"	NaCl	9.46	0.0

In this experiment it was apparent, as in preceding ones, that the absorption of potassium from the solution of the second period was strikingly decreased when sodium was present in the solution of the first period.

The procedure employed in this paper, using the plant itself as an indicator, and transferring it from soil to solution or from one solution to another, together with the delicate analytical methods which made it possible to measure slight changes in the concentration of the solution, would seem to be applicable to the study of certain phases of the most important agricultural problems.

BUREAU OF SOILS,  
U. S. DEPARTMENT OF AGRICULTURE,  
WASHINGTON, D. C.

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## REACTIONS OF ACETYLENE WITH ACIDIFIED SOLUTIONS OF MERCURY AND SILVER SALTS.

BY J. A. NIEUWLAND AND J. A. MAGUIRE.

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FROM work already published on the behavior of acetylene towards neutral and acid solutions of mercury and other metals, it is fair to conclude that there is a possibility of forming compounds other than those already mentioned. Up to the present time the only acetylene derivatives of mercury that have been investigated are the nitrates (mercurous and mercuric), the chloride, bromide and the fluoride. It was expected that with acid solutions such as mercury fluosilicate, fluoborate, cyanide, nitrite, chlorate and perchlorate, compounds analogous to those discussed in the previous work,<sup>1</sup> would be formed under proper conditions.

While the work to be described was in progress there came to our notice an article of Hoffman<sup>2</sup> in which, among other compounds, he described the formation of acetylene derivatives of mercuric nitrite, chlorate and perchlorate. His method of preparing these substances is almost identical with the method by which we made them. Besides the substances mentioned by Hoffman, we have been working on a number of others about to be described. The general method of procedure was to make

<sup>1</sup> Thesis: "Some Reactions of Acetylene," Notre Dame University Press, 1904.

<sup>2</sup> Ber. 38, 1899.

the solution of a salt of mercury by treating the acid in question with mercuric oxide and filtering. Care was taken to have these solutions acidified with the acid contained in the radical of the salt. The product was treated with purified acetylene gas that had passed through three Wolff flasks containing in the order mentioned: first, a solution of caustic potash; second, chromic acid; third, some sulphuric acid. The gas was also passed through a drying tower containing small pieces of calcium carbide. The following results were obtained:

*Acetylene and Mercuric Chromate.*—In a solution of mercuric chromate acidified with chromic acid, acetylene gave instantaneously a bright yellow precipitate resembling lead chromate. The acid solution of the salt was obtained in the following way. To a cold concentrated solution of chromic acid, oxide of mercury was added until no more was dissolved on shaking. After filtering the solution through asbestos, acetylene was passed into it until a precipitate was no longer formed with the gas. The compound was carefully washed for a long time both by decantation and filtration to remove the last traces of chromic acid, and the precipitate dried over sulphuric acid. But in spite of all possible care used in the process of drying, the substance turned brown, aldehyde being one of the products of decomposition. With moist iodine the compound yielded iodoform, especially in an alkaline solution, and when rubbed in a mortar or touched with a warm glass rod, deflagration took place without explosion, and carbon together with the oxide of chromium was deposited. Ordinary acids did not perfectly dissolve the chromate derivative of acetylene, but it readily went into solution in a mixture that yielded nascent chlorine. The following results were obtained in the analysis for mercury:

0.4546 gram of substance gave 0.3736 gram of mercuric sulphide.

0.4062 gram of substance gave 0.3392 gram of mercuric sulphide.

	Calculated for (OH)C   HC > Hg <sub>2</sub> CrO <sub>4</sub> .	Found.	
		I.	II
Hg.....	70.42	70.85	71.12

*Acetylene and Mercuric Fluosilicate and Fluoborate.*—Mercury silicofluoride was prepared by dissolving mercuric oxide in fluo-

silicic acid to saturation. After filtering and passing in acetylene, a white precipitate was formed which towards the end of the reaction began to turn blue, while the odor of aldehyde was very strong. The same results were obtained when acetylene was passed into the fluoborate. These compounds are very unstable, decomposing spontaneously even when dry, into aldehyde and hydrofluoric acid. They respond to the iodoform reaction more readily than any of the other derivatives of acetylene formed in a similar manner. They reacted energetically with dry bromine and chlorine, apparently forming bromine and chlorine substitution products of ethane. Strong hydrochloric acid attacked them, with the formation of the hydrochloride referred to by Keiser<sup>1</sup> and prepared by Polleck and Thummel<sup>2</sup> in another way. It

was expected that the following compounds, 
$$\begin{array}{c} (\text{OH})\text{CHg} \\ | \\ \text{H}.\text{CHg} \end{array} \text{SiF}_6 \text{ and } \begin{array}{c} (\text{OH}).\text{C}.\text{(HgBF}_4\text{)} \\ | \\ \text{H}.\text{C}.\text{(HgBF}_4\text{)} \end{array}$$
, would be obtained, but a qualitative analysis

shows, however, that the boron and the silicon of the acids either took no part in the reaction, or were removed by the acetylene, so that the same substance is formed as in the reaction of acetylene with mercuric fluoride. Quite a number of analyses were made but no satisfactory coincident results could be obtained.

*Acetylene and Mercuric Chlorate and Perchlorate.*—Chemically pure chloric acid was prepared from pure barium chlorate by precipitation with sulphuric acid. Mercuric oxide was dissolved in the acid and acetylene passed into the solution. The white precipitate formed was washed and dried in small quantities over sulphuric acid in a desiccator. Great care had to be used in handling this compound as it was extremely explosive both on contact with sulphuric acid and by percussion or friction. When heated even the smallest quantities detonated with great violence. It gave acetaldehyde on standing in contact with water, and gave the iodoform reaction both with and without alkalis. It decomposed paper and other organic substances, and dissolved in all the acids. It does not explode in the wet state, but slowly decomposes.

Perchlorate of mercury was made from pure perchloric acid and

<sup>1</sup> Am. Ch. J. 15, 535.

<sup>2</sup> Ber. 22, 2863 (1889).

mercuric oxide. The perchlorate of mercury and acetylene resembles the chlorate in every respect, except that it did not explode with sulphuric acid when the compound was washed for a long time, nor even when heated or rubbed in a mortar. The least trace of chloric acid or of mercuric perchlorate in the free state caused violent explosions when thus treated. Analysis of these compounds gave similar erratic results as in the case of the fluosilicate and fluoborate.

*Acetylene and Mercuric Cyanide.*—When pure acetylene was passed into a solution of mercuric cyanide, made acid with hydrocyanic acid, no precipitate was obtained. If, however, the impure gas that had not been passed through water or sulphuric acid was used, a cream colored precipitate was formed after a few days. As ammonia was given off from the decomposition of the calcium carbide, the solution was slowly made alkaline, causing a precipitate of mercuric carbide. Not enough of the substance was obtained for analysis or thorough examination. The compound was explosive and hence was supposed to be a carbide.

*Acetylene and Mercuric Nitrite.*—Acetylene gave a heavy cream colored precipitate with mercuric nitrite. If the solution of the nitrite is fairly strong, the reaction after a while becomes so energetic as to give off sufficient heat to effect the decomposition of the compound with the evolution of nitrous fumes and at the same time aldehyde is given off in considerable quantities. In a concentrated solution of nitrous acid and mercuric nitrite, the organic compound is very soluble but can be precipitated by dilution with water. Like the other compounds the nitrite gave an abundant precipitate of iodoform with iodine and an alkali. Analysis of the compound gave the following results:

0.8000 gram of the substance gave 0.7129 gram of mercuric sulphide.

0.4598 gram of the substance gave 0.4100 gram of mercuric sulphide.

	Calculated for C—(HgNO <sub>2</sub> ) C—(HgNO <sub>2</sub> )	Found.	
		I.	II.
Mercury.....	77.51 per cent.	76.80	74.49

*Acetylene and Mercuric Acetamide.*—Acetylene gave a white gelatinous precipitate with mercuric acetamide. Mercuric acetamide was made, by dissolving mercuric oxide in an aqueous solution of acetamide, also by melting acetamide, adding the

oxide, and then diluting with water. The substance was found to be of the consistency of jelly, if little or no water was added to the acetamide.

*Acetylene and Mercuric Bromate.*—Mercuric bromate was made from pure bromic acid and mercuric oxide. It gave a very explosive white precipitate with acetylene, which was not analyzed, whereas the iodate of mercury could not be obtained in the same way.

The general properties of the above compounds may be summed up as follows: Whereas the carbides formed from acetylene in alkaline solutions are explosive, the substances formed in acid solutions are not necessarily explosive unless there is in the compound an acid grouping or radical that is itself unstable, such as that of chloric or perchloric acid. The chromic acid radical, though a strong oxidizing agent, is not violently decomposed when combined with the acetylene, though it is rather unstable. All of these compounds give off aldehyde when heated with very dilute acids or even with water. Some decomposed thus, even when kept perfectly dry in a desiccator over sulphuric acid or in tightly closed bottles. Caustic alkalis break up these compounds into two others, one soluble, the other insoluble in the reagent. The product insoluble in the alkali when treated with iodine, gave tetraiodoacetylene and diiodoacetylene, and resembled the carbide of acetylene, being somewhat explosive. The other substance, soluble in fixed alkalis, is reprecipitated by acidifying the solution containing it. It is the compound which gave the iodoform reaction. These, and other considerations seem to point to the fact that they are substances like those obtained by Polleck and Thümmel<sup>1</sup> by another reaction from vinyl derivatives. Therefore, we have preferred to consider them as derivatives of vinyl alcohol and not of aldehyde. Moreover, if they were acetaldehyde derivatives, the aldehyde, if it reacted with the salts of mercury, should give these compounds. Acetaldehyde forms soluble, not insoluble compounds in presence of mercury salts.

*Acetylene and Acidified Silver Phosphate.*—Silver like mercury, gave insoluble products with acidified solutions. The compounds formed from acid silver fluoride, acid fluosilicate and acid fluoborate, and from solutions of silver chloride in sodium hy-

<sup>1</sup> Loc. cit.

posulphite, are yellowish precipitates and are all explosive. Silver chromate, though slightly soluble in potassium bichromate and chromic acid, would not give a precipitate with acetylene. Other silver compounds have been prepared from acidified solutions.

Unlike these substances, acid silver phosphate of acetylene is not explosive, in fact it is very stable and only slowly acted upon by light. The solution of silver phosphate was prepared by precipitating from a solution of silver nitrate with disodium phosphate, and dissolving the precipitate in rather strong phosphoric acid. When acetylene was passed into the solution a cream colored substance was thrown down. The silver was quantitatively precipitated, and after saturating with acetylene, no trace of the metal could be found in the solution, which was found to be unchanged phosphoric acid. Light affected the compound only very slowly, for after standing for several months in strong diffused daylight, the color was changed only to a faint lavender. The compound did not give off aldehyde, nor did it respond to the iodoform reaction. It was soluble in potassium cyanide with evolution of acetylene and gave off the odor of hydrocyanic acid. When heated it did not explode, but puffed up, decomposing slowly, leaving finely divided carbon and silver. This substance appears in this respect, to differ from all the silver acetylene derivatives. Analysis of the compound pointed to the following composition. The silver was determined electrolytically, and there was found 44.77 and 44.77 per cent. Calculated for  $3(\text{C}_2\text{H}_2)$ ,  $2\text{H}_3\text{PO}_4 \cdot \text{Ag}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , 45.3 per cent.

*Other Silver Acetylene Compounds.*—Besides the acetylene compound of silver phosphate, other derivatives were prepared. When acetylene gas was passed into an acidified solution of silver fluoride, a lemon-yellow precipitate was formed. The substance is paler in color when formed in dilute solution. It is extremely explosive and is probably a compound of silver carbide with silver fluoride. Silver nitrite yields a compound similar in appearance and physical properties. No results could be obtained when acetylene was passed into acidified silver chromate. No compound of silver cyanide and acetylene could be prepared. Silver cyanide was precipitated, washed carefully and redissolved in potassium cyanide. Acetylene gave no precipitate when passed into the solution to which some hydrocyanic acid had been added. The compounds of acetylene with silver bromate

and silver perchlorate were also made. The gas formed precipitates in solutions of these salts acidified with pure bromic and perchloric acids respectively. The perchlorate was prepared by dissolving silver oxide in pure concentrated perchloric acid. Care was taken to have the silver salt strongly acid. When acetylene gas was passed in the solution, a fine crystalline precipitate was obtained. This substance, even in the moist condition, is almost as explosive as nitrogen iodide. On one occasion simple contact of the wet substance with a glass rod resulted in an explosion that shattered the vessel. No smoke or precipitate of carbon accompanies these explosions, thus differing in this respect from the other silver acetylene compounds. These detonations are accompanied with a flash of pale blue light. The smallest quantities of the substance are dangerous. The amount that usually "creeps" up the sides of the vessel in the preparation of the compound, has been known to pulverize the containing beaker when touched with a glass rod. The product formed in very dilute solution is, however, not quite so explosive. Owing to the dangerous nature of this compound, no analysis was attempted. None of the silver compounds of acetylene give the iodoform reaction, and all except the phosphate are quickly blackened by diffuse daylight. Investigation of other metallic derivatives of acetylene is now being made in the laboratory.

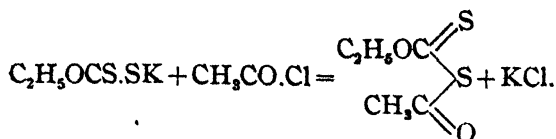
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### NOTES.

*A Preliminary Note on the Reactions between Acid Chlorides and Potassium Ethylxanthate.*—In the spring of 1902 the author undertook to study the action of various acid chlorides on potassium ethylxanthate,  $C_2H_5OCS.SK$ . Owing to press of other work this study has been subject to numerous delays and postponements; it has therefore been deemed advisable to make a preliminary announcement of the work done.

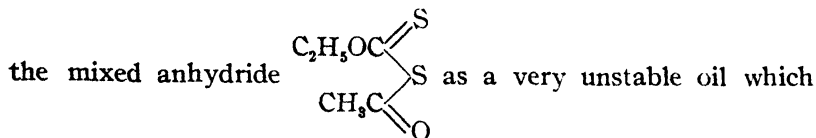
*Action of Acetyl Chloride.*—The products obtained by the action of acetyl chloride on potassium ethylxanthate vary with slight changes in conditions. Ideally, there should be obtained the mixed anhydride of ethylxanthic and acetic acids according to the reaction





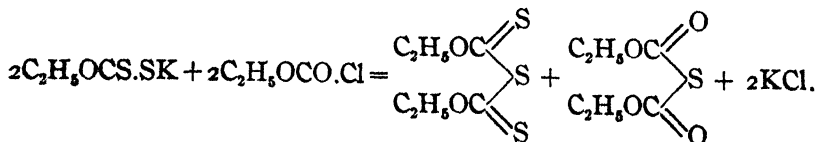
On heating, two molecules of ethylxanthoacetic anhydride should break up to give one molecule of ethylxanthic anhydride and one of thioacetic anhydride according to the well-known rule obtaining with mixed anhydrides of the fatty acids. In practice, however, the reaction takes different courses according to conditions, giving products all of which have not yet been identified with certainty.

When acetyl chloride is added to a well-cooled flask containing potassium ethylxanthate suspended in much ether, there is formed



on moderate heating decomposes, not into the simple anhydrides one would expect, but into ethyl acetate, carbon disulphide, and other products. When, however, potassium ethylxanthate is treated with acetyl chloride in the presence of but small amounts of solvent and without cooling, the reaction takes to some extent the normal course; in this way ethylxanthic anhydride was obtained in fairly large amount. The substance was identified by its melting-point ( $54^\circ$ ), by its properties as described by Welde,<sup>1</sup> and by a sulphur determination which gave 45.91 per cent. S; calculated for  $(\text{C}_2\text{H}_5\text{O})_2\text{C}_2\text{S}_3$ , 45.71 per cent.

*Action of Chlorcarbonic Ester.*—Chlorcarbonic ester and potassium ethylxanthate react with energy. Besides potassium chloride there is obtained an oil containing ethylxanthic anhydride in solution in smaller amount than one would expect from the reaction:



After complete removal of ethylxanthic anhydride from the

<sup>1</sup> J. pr. Chem. [2] 15, 45.

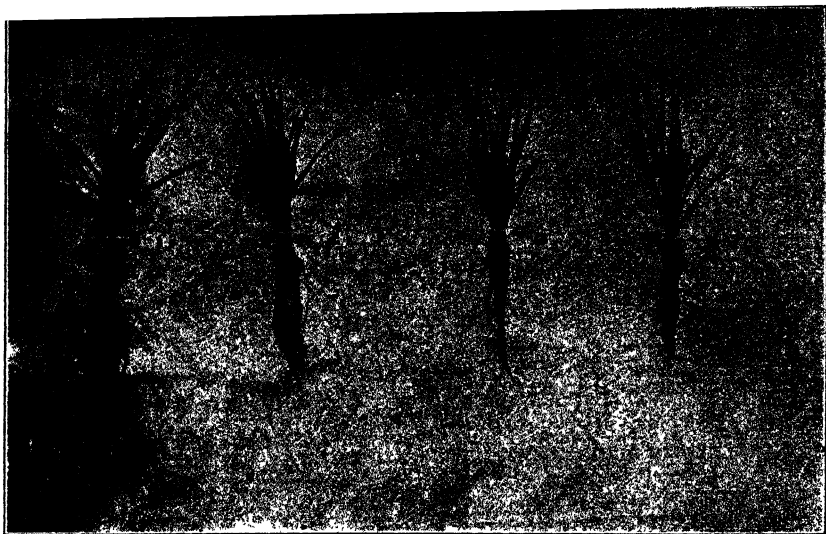


Fig 1.

No. 1—Full nutrient solution No. 2—Nutrient without sodium No. 3—Nutrient without potassium No. 4—Nutrient without both sodium and potassium.

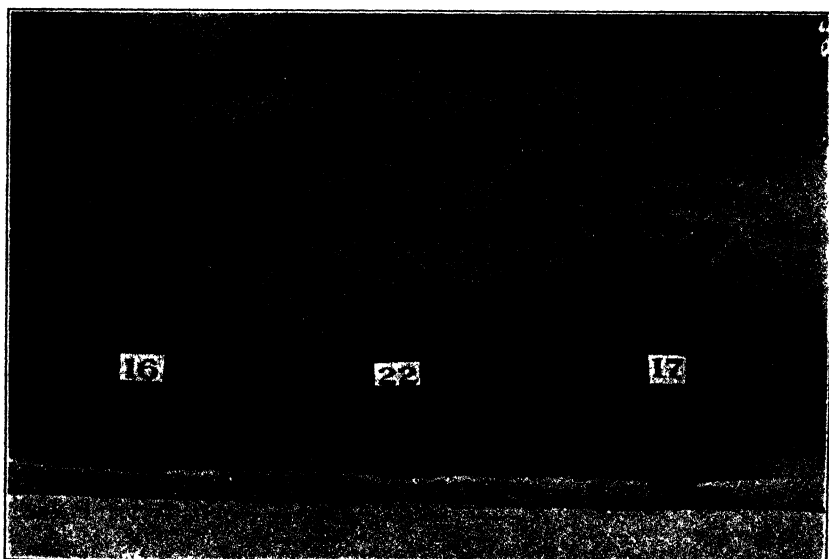


Fig 2.

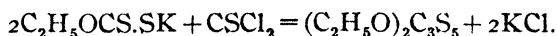
Treatment. Plot No. 16—200 lbs per acre of sodium chloride; 160 potassium chloride. Plot No. 22—No sodium chloride. 362 lbs per acre of potassium chloride. Plot No. 17—200 lbs. per acre of sodium chloride; 362 lbs per acre of potassium chloride.



oily reaction product there is left a complex mixture which has not yet been completely resolved into its constituents.

It is not unlikely that an exhaustive study of these reactions will reveal evidence of the temporary existence of interesting dissociation products, and it is from this standpoint that the reactions will be studied when the work is resumed.

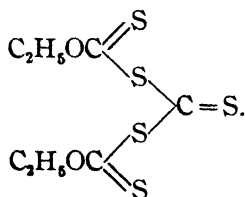
*Action of Thiophosgene,  $\text{CSCl}_2$ .*—To the calculated amount of thiophosgene contained in a small flask was added an ice-cold water solution of potassium ethylxanthate in proportion to satisfy the equation:



The water solution became slightly turbid at once, but no further action appeared to take place. The flask was put away in a cool place and occasionally shaken. The lower layer of thiophosgene gradually lost its mobility, becoming finally a dark-brown waxy mass. The water was then poured off and the waxy mass extracted with boiling alcohol. This treatment left undissolved a white crystalline solid soluble in benzene, from which it was recrystallized. Analysis gave the following results: 0.1426 gram substance gave 0.5810 gram  $\text{BaSO}_4$  (Carius' method). 0.3444 gram substance gave 0.3582 gram  $\text{CO}_2$  and 0.1045 gram  $\text{H}_2\text{O}$ .

	Calculated for ( $\text{C}_2\text{H}_5\text{O}$ ) <sub>2</sub> $\text{C}_3\text{S}_5$ . Per cent	Found. Per cent.
C .....	29.37	28.36
H .....	3.49	3.37
S .....	55.94	55.93

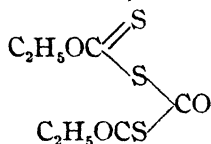
This substance is probably the diethyl ester of the hypothetical pentathiotricarbonic acid,  $\text{C}_3\text{S}_5(\text{OH})_2$ :



It crystallizes from hot benzene in microscopic crystals: it melts with decomposition at  $160^\circ$ , and is quite stable toward dilute acids and alkalis. Hot concentrated sulphuric acid decomposes it with liberation of much sulphur. The same substance is immediately precipitated along with potassium chloride

when thiophosgene diluted with acetone is added to an acetone solution of potassium ethylxanthate. The acetone filtrate yields on evaporation a thick, yellowish-brown oil of unknown composition.

*Action of Phosgene,  $\text{COCl}_2$ .*—From analogy with the result obtained as described above, it was expected that the diethyl ester of the hypothetical tetrathiotricarbonic acid,  $\text{C}_3\text{S}_6\text{O}(\text{OH})_2$ , would be obtained when phosgene in toluene solution was allowed to act on potassium ethylxanthate; however, none of the compound



was obtained. The reaction is apparently complex. Ethylxanthic anhydride in large amount was found in the reaction product.

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*Carborundum and Siloxicon.*—I have read with considerable interest the account of experiments conducted by Messrs. S. A. Tucker and Alexander Lampen on the measurements of temperature in the formation of carborundum, which appeared in this Journal in its July number.

The methods pursued by them were ingenious, but I would say that the temperature they arrived at was somewhat lower than I had anticipated, although I had not made any definite measurements relating to them.

There seems to be, in the text of their article, some confusion regarding siloxicon. This word I coined as a name of a silicon-oxygen-carbon compound and not for amorphous silicon carbide, as stated by them. The zone of material immediately surrounding carborundum (crystalline carbide of silicon) is mainly or wholly composed of an oxygen compound with carbon as an impurity, this carbon being eventually utilized for the extraction of the residual oxygen and formation of a definite silicon carbide. While this apparent inaccuracy does not in any way detract from the interest and value of their determinations, I can scarcely let such a positive statement of the chemical composition of siloxicon pass unnoticed.

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## REVIEWS.

### REPORT OF THE INTERNATIONAL COMMITTEE ON ANALYSIS TO THE SIXTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY AT ROME, 1906.<sup>1</sup>

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Received June 18, 1906

THE International Committee on Analysis appointed by the Fifth International Congress of Applied Chemistry (Berlin, 1903) and subsequently enlarged by the addition of new members selected by the original committee, was composed of 43 members representing 18 different countries. This committee was divided into 11 sub-committees, to which 14 questions were assigned as follows:

(I) (1) Uniform methods for the determination of lead, copper, silver, antimony and zinc.

(II) (2) Uniform materials for use as standards in volumetric analysis, and directions for purifying them and preparing them for weighing.

(3) Uniform manufacture of reagents.

(III) (4) Uniform principles relating to the adjustment and calibration of chemical measuring apparatus.

(8) Uniform principles concerning the adjustment and calibration of instruments for density and percentage determinations.

(9) Adjustment and legalization of balances and weights for chemical purposes.

(IV) (5) Methods of sampling materials for analysis.

(V) (6) Accurate statement of results obtained in fuel investigation.

(VI) (7) Uniform presentation of analytical results.

(VII) (10) Determination of arsenic in wall papers, fabrics, etc.

(VIII) (11) Determination of boric acid, benzoic acid, salicylic acid and other substances employed in the preservation of foods.

(IX) (12) Determination of sulphur in pyrites, blendes, etc.

(X) (13) Is it necessary to calculate the percentage of manganese in a permanganate solution the strength of which with respect to iron is known, by means of a coefficient different from that indicated by the equation?

(XI) (14) Methods of analyzing materials containing tartaric acid.

The statement is made by Dr. G. Lunge, chairman of the committee and editor of the report, that the work upon questions 2, 12 and 13 may be considered complete, or nearly complete;

<sup>1</sup> Edited by Dr. G. Lunge. Pages iv+421. Zurich, 1906. Zürcher & Furrer.

that the work upon questions 1, 4, 5, 6, 7, 8, 9, 10 and 11 has led to the accumulation of much valuable material, but has not yet culminated in the establishment of uniform methods; that one member of the committee only has in each case reported upon questions 5 and 8, and that question 3 has received no attention whatever.

*Sub-Committee I. Question 1. Uniform Methods for the Determination of Lead, Copper, Silver, Antimony and Zinc.* (Pages 16-70.)—The work in this field has by no means led to the establishment of uniform methods. Considerable progress toward this goal has, however, been made in the study of methods for the determination, respectively, of zinc and of copper. The report embraces (A) a brief general discussion (by G. Chesneau, chairman of the first sub-committee) of the methods usually employed for rapid work in industrial laboratories, or for accurate work in scientific laboratories, together with a brief resumé of the experimental work performed by members of the sub-committee; (B) a discussion, both historical and experimental (by H. Nissenson and W. Kettembeil) of the methods employed in the determination of zinc; (C) an article (by Nissenson) on the importance of uniform, international methods of analysis; (D) a study of the electrolytic method for determination of copper (by A. Menozzi); and (E) a communication (by Nissenson) concerning the methods of assaying employed in the Central Laboratory of the Stock Company at Stolberg. A brief statement of some results obtained in the work upon the determination of zinc and copper should be of general interest.

*On the Determination of Zinc.*—Two volumetric methods are commonly employed in technical laboratories: titration with sodium sulphide solution, and titration with potassium ferrocyanide solution. The authors propose a slight modification of the latter method as employed by de Koninck and Prost (*Z. angew. Ch.* 1896, 460-468; 564-572). Instead of adding an excess of potassium ferrocyanide at the outset, and then titrating back the cold solution with a standard zinc solution, the authors titrate directly, heating the solutions in order to hasten the reaction. They employ a 1 per cent. solution of uranium nitrate as indicator, but find that a solution of ammonium molybdate containing 9 grams to the liter serves as a satisfactory indicator, reacting more rapidly than the uranium solution, and to certain observers offering a sharper end-point. A comparison of the results obtained by the use of the sodium sulphide method and the ferrocyanide method respectively, shows them to be remarkably concordant. Both methods are also shown to give results agreeing very closely with results obtained both with the gravimetric (precipitation with hydrogen sulphide) method and with Nissenson's (*Z. Elektrochem.* 9, 761 (1903); *Chem. Ztg.* 27, 659

(1903)) electrolytic method. Sufficient practical work has not yet been performed to warrant the selection for international use of either method in preference to the other.

The determination of zinc in scientific laboratories is in general accomplished by precipitating the zinc with hydrogen sulphide, preferably from a warm solution acidified with acetic or formic acid. The final treatment of the zinc sulphide obtained is subject to considerable variation in different laboratories. The remarkable agreement obtained by Nissenson between the results from the gravimetric and the electrolytic methods respectively, seems to point toward the latter as the standard method of the future.

For the complete analysis of metallic zinc several different methods have been in use. The method recommended by Nissenson is briefly as follows: 100 grams of the metal are placed in a 750 cc. Erlenmeyer flask provided with a safety tube, and are treated with about 200 cc. of water. Sufficient sulphuric acid is gradually added to maintain a slow evolution of gas. This gas is led into a small Erlenmeyer holding 10 cc. of a solution that contains 7 grams of bromine and 7 grams of sodium hydroxide per liter. When the zinc has almost entirely dissolved, the remaining spongy material is filtered off, and washed until all sulphuric acid has been removed. The amount of iron in the filtrate is determined by titration with permanganate. The spongy material is dissolved in nitric acid. A precipitate at this point may be caused by tin or by large amounts of antimony. If no precipitate appears, the solution is treated with 12 cc. of dilute sulphuric acid, and evaporated until white fumes appear. After the separation and determination of the lead, the filtrate is warmed and treated with hydrogen sulphide. The precipitate is filtered off, allowed to stand in a cold solution of sodium sulphide for some time, and is filtered. In the filtrate antimony is precipitated with sulphuric acid, allowed to subside, filtered off, and dissolved in concentrated hydrochloric acid. The solution is boiled until all hydrogen sulphide is expelled, treated with from 15 to 20 cc. of dilute hydrochloric acid, and is titrated while boiling hot with potassium bromate, indigo being used as indicator (*Berg. hüttenmänn. Ztg.* 62, 421 (1903)). The residue left after the above-mentioned treatment with sodium sulphide is dissolved in nitric acid. The solution is almost neutralized with ammonium hydroxide, and is treated with ammonium carbonate until it reacts alkaline. After it has been standing (warm) for several hours the bismuth carbonate is filtered off and is dissolved in a few drops of sulphuric acid. The solution is evaporated until white fumes appear in order to remove the last traces of lead. The bismuth is once more precipitated, and is finally determined as  $\text{Bi}_2\text{O}_3$ . If copper is present in the filtrate from the first bismuth precipitate, this solution is decolorized with potassium cyanide.



Cadmium is precipitated with sodium sulphide, is filtered off and is weighed as  $\text{CdO}$ , while from the filtrate copper sulphide is precipitated by cautious addition of acid. The filtrate from the hydrogen sulphide precipitate is boiled to expel hydrogen sulphide, is oxidized and is treated with ammonium hydroxide. Iron is determined after a second precipitation. The filtrate from the first iron precipitate is acidified, and is treated (hot) with a few drops of barium chloride solution. The barium sulphate is removed by filtration. The barium remaining in the filtrate is precipitated with sulphuric acid, and is filtered off. The hot solution is treated with hydrogen sulphide. The arsenious sulphide is filtered off, and if it still contains antimony is treated with cold ammonium carbonate. The solution is again filtered. The arsenic in the filtrate is precipitated with dilute sulphuric acid, is filtered off, and after being dissolved in hydrochloric acid, to which some potassium chlorate has been added, is precipitated with magnesia mixture. This method is commendable in that a single 100-gram sample suffices for the determination of all ordinary impurities and in that provision is made for the determination of bismuth, an operation that has been neglected by authors of previously published methods. Nissenson believes that the percentage of zinc itself is best determined by difference. Chesneau, however, cautions chemists against the extension of this indirect method to other cases, however applicable it may in the case of zinc. He is of the opinion that the percentage of each impurity and the percentage of the metal itself should in each case be directly determined.

*On the Electrolytic Determination of Copper.*—This subject is discussed by A. Menozzi who has made an experimental study of the various conditions governing the deposition of copper for analytical purposes. The negative electrodes employed in the work comprised two platinum dishes with a capacity of from 100 to 150 cc., with an inside surface of from 100 to 125 sq. cm., and weighing from 60 to 62 grams; two cones with a working surface of 160 sq. cm., and weighing from 22 to 29 grams; a cylinder with a total surface of 260 sq. cm., weighing a little over 54 grams, and a cylinder of platinum gauze, with a surface of about 145 sq. cm., weighing 12 grams. Platinum spirals, discs and gauzes served as positive electrodes. Especial emphasis is laid upon the desirability of employing the rotating anode. For this work the electrodes of Classen are well adapted, while the gauze electrodes of Winkler are unsatisfactory. The stirring apparatus of Fischer and Boddaert was employed. The author's results may be summarized as follows: (A) Deposition from acid solution. A nitric or sulphuric acid solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. From 2 to 5 volumes of concentrated nitric acid or from 3 to 5 volumes of sulphuric acid are added to 100 volumes of

the electrolyte. The mean tension of the current for ordinary electrolysis should be from 1 to 3 volts; for electrolysis with rotating electrode, from 3 to 4 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 ampere; for electrolysis with rotating electrode, from 4 to 5 amperes. The presence of an excess of nitric acid, or of chlorides, organic acids, arsenic, antimony, bismuth, mercury, silver or tin, is detrimental. Agitation of the liquid (by rotating electrode) remarkably facilitates the deposition of the copper. Heating the electrolyte favors the deposition of copper, but if the temperature is raised too high, removal of the last traces of copper becomes almost impossible. The deposit must be rinsed with water, alcohol, and alcohol and ether, without interrupting the current. The deposition requires from three to twelve hours when the ordinary method is employed; with the rotating electrode it requires about one hour. The end-point may be determined by testing the electrolytic solution for copper by the usual chemical methods, or by means of an auxiliary electrode. Copper may be separated by the electrolytic method from alkali and alkaline earth metals, from zinc, cadmium, nickel, cobalt, aluminum, chromium, iron (if present in small quantities) and from lead and manganese (in presence of an excess of nitric acid). One of the principal difficulties connected with the electrolytic precipitation of copper is to obtain, in acid solution, a complete deposition of the last traces of the metal. Some laboratories overcome the difficulty by concentrating the solution toward the end. Menozzi prefers to determine the residual copper colorimetrically, after treating the solution with ammonium hydroxide.

(B) Deposition from alkaline solution. A nitrate, sulphate or chloride solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. Sufficient ammonium hydroxide is added to redissolve the precipitate at first formed. Then more ammonium hydroxide (0.96) is added, from 20 to 25 cc. for a solution containing 0.5 gram of copper, and from 30 to 35 cc. for a solution containing 1 gram of copper. From 3 to 4 grams of ammonium nitrate are also added. The mean tension of the current for ordinary electrolysis is from 2 to 4 volts; with rotating electrode it is from 3 to 5 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 amperes; with rotating electrode it is from 4 to 5 amperes. The presence of lead, bismuth, mercury, cadmium and nickel is detrimental. Agitation of the liquid (by rotating electrode) accelerates the deposition of copper. Heating is to be avoided. The deposited metal should be washed without interrupting the current. Precipitation requires from four to twelve hours by the ordinary method; with the rotating electrode it requires from one to two hours. The action may be considered complete when the solution has completely lost its color.

*Sub-Committee II. Question 2. Uniform Materials for Use as*

*Standards in Volumetric Analysis, and Directions for Purifying Them and Preparing Them for Weighing.* (Pages 71-153.)—The report of work accomplished in this field embraces a general statement by W. Fresenius (chairman of the second sub-committee), and two articles of considerable length already published elsewhere ("Beiträge zur chemisch-technischen Analyse," *Z. angew. Ch.* **17**, 195-203; 225-236; 265-270 (1904). *Centrbl.* 1904, I, 1036. "Zur Frage der Einstellung von Normalsäuren für Massanalyse," *Z. angew. Ch.* **18**, 1520 (1905); *Chem. Centr.* 1905, II, 1284) by G. Lunge. Other articles published ("Zur Frage über einheitliche Titersubstanzen (Urtitersubstanzen)," S. P. L. Sørensen, *Z. anal. Ch.* **44**, 141 (1905); "Über die Anwendung von Natriumkarbonat und Natriumoxalat in der Acidimetrie," S. P. L. Sørensen und A. C. Anderson, *Z. anal. Ch.* **44**, 156 (1905), **45**, 217 (1906); "Zur Frage der Titerstellung von Normalsäuren," J. Sebelien, *Chem. Ztg.* **29**, 638 (1905)) by members of this sub-committee have been briefly reviewed in the chairman's report. In the opinion of W. Fresenius it may now be regarded as an established fact that either sodium carbonate (when prepared according to Lunge's directions) or sodium oxalate (ignited either over an alcohol flame, or a gas flame so applied that the products of combustion cannot come into contact with the salt) may be employed as standard materials for use in acidimetry, even in work requiring a high degree of accuracy.

*Preparation of Sodium Carbonate for Use in Standardizing Acid Solutions.*—The material selected should be of a pure white color, and should dissolve in water forming a perfectly clear solution. In quantities of from 1 to 2 grams it should give no reaction for sulphates, and with silver nitrate should give no more than the faintest opalescence. By heating, it is possible to insure the removal of water, and of any excess of carbon dioxide that may be present. If the temperature is too high,  $\text{Na}_2\text{O}$  may be formed. The fortunate circumstance that there is a considerable range of temperature through which the material may be heated without danger, gives to sodium carbonate the preference (according to Lunge) over all other substances hitherto suggested as the basis for standardization of acids. A platinum dish half filled with the material is so placed upon a sand-bath that the sand surrounds it to the height of the sodium carbonate within. The heating should be rapid until the temperature of  $270^\circ$  is reached, when it should be continued more slowly for one-half hour, during which time the temperature should not be permitted to rise above  $300^\circ$ . During this process the substance should be frequently stirred with a platinum spatula or with a flattened glass rod.

*Preparation of Sodium Oxalate for Use in Standardizing Acid Solutions.*—According to Sørensen's directions, the material is first precipitated with alcohol and dried at  $240^\circ$ . The sodium oxalate employed in the experiments of Lunge was obtained from

Kahlbaum, who had prepared it in this way. In order to obtain the greatest accuracy it is advisable to dry the salt in a water-bath drying-closet for some time before weighing. Lunge dried the salt for two and one-half hours, and then allowed it to cool in a desiccator for two hours. About 0.5 gram of the sodium oxalate is now weighed out into a platinum crucible provided with a cover, and is heated until complete transformation to sodium carbonate takes place. In one-fourth to one-half hour, according to Lunge, the change is complete, but the crucible should then be heated to a higher temperature in order to oxidize the small quantity of carbon liberated during the process. During this last operation the crucible should be left partly uncovered. As source of heat should be employed either an alcohol flame or a gas flame so applied that the products of combustion cannot come into contact with the salt. According to Lunge, the crucible should be set upon an asbestos plate through which a hole of proper size has been cut. If this precaution is not taken, the sulphur compounds in the illuminating gas will react with the sodium carbonate, introducing an appreciable error in the final result. After the ignition has been completed, the sodium carbonate is moistened with water and is then treated with the acid to be standardized.

The use of methyl orange as indicator is recommended in all cases except those in which a weak acid is involved. Phenolphthalein gives a sharper end-point, but necessitates a more complicated procedure. The nitrophenols and ferric salicylate show no superiority over methyl orange.

Pure iodine is still recommended as the basis of iodometric titrations. Potassium biiodate of constant composition may not be readily prepared. For the standardization of potassium permanganate Lunge has found that with certain precautions any one of the four following substances may be employed: (1) oxalic acid, (2) iron wire, (3) sodium oxalate and (4) hydrogen peroxide (by the nitrometer method).

*Sub-committee III. Question 4. Uniform Principles Relating to the Adjustment and Calibration of Chemical Measuring Apparatus.*—The report upon this subject consists in a series of regulations (stated in German, French and English) classified as follows:

*International regulations concerning chemical measuring apparatus.*

I. Measuring Vessels for Volumetric Analysis.

- A. General Rules.
- B. Shape and Calibration.
- C. Particular Rules.
- D. Limits of Error.

II. Measuring Apparatus for Gas Analysis.

- A. General Rules.

## B. Shape and Calibration.

## C. Limits of Error.

*Question 8. Uniform Principles Concerning the Adjustment and Calibration of Instruments for Density and Percentage Determinations.*—Under this head is given (in German, French and English) a series of regulations classified as follows:

*International Regulations Concerning Hydrometers.*

## A. General Rules.

## B. Shape and Calibration.

## C. Special Hydrometers.

## D. Limits of Error.

*Question 9. Adjustment and Legalization of Balances and Weights for Chemical Purposes.*—The report upon this subject presented by H. W. Wiley contains an account, both historical and descriptive, of the United States standards of weight and measure, together with a brief statement concerning the purpose of the Bureau of Standards. Reference is made to the method of T. W. Richards (this Journal, 22, 144 (1900)) for standardizing weights.

*Sub-committee IV. Question 5. Methods of Sampling Materials for Analysis.* (Pages 190-220.)—The chairman of the fourth sub-committee, Dr. H. W. Wiley, has presented a report containing a detailed discussion of the topics mentioned in the following summary:

*Part I. General Principles of Sampling.*—(Applied to the sampling of gases, liquids and solids.)

*Part II. Sampling Special Classes of Materials.*

*Soils.*—General principles. General directions for sampling. Sampling with an auger. Sampling for moisture determination. Sampling to determine the permeability of soil to water or air. *Treatment of sample.* Air-drying.

*Fertilizers.**Minerals Containing Fertilizing Materials.**Mixed Fertilizers. Barn-yard Manures.**Materials used for Road Building.*

*Food Products.*—Dairy products (butter, milk and cheese). Sugars and molasses. Cattle foods. Insecticides. Foods. Drugs and chemicals (including (1) gummy substances, (2) powders, (3) crude vegetable drugs, (4) liquids, (5) goods solid at ordinary temperatures, but liquefied on warming, and (6) articles that congeal in part or as a whole at low temperatures.)

*Sub-committee V. Question 6. Accurate Statement of Results Obtained in Fuel Investigation.* (Pages 221-225.)—A brief and incomplete discussion of several questions bearing upon the analysis and testing of fuels. Among these questions may be mentioned the following: In what way may the results of a fuel examination be most intelligibly expressed? For example, should the higher or the lower heating value be reported; should

the percentages of hydrogen and oxygen be directly reported, or should they be calculated as available hydrogen and chemically combined water? In what way should the percentage of sulphur found by analysis of the coal be reported? Should the amount of water formed by combustion of the coal be determined directly from combustion in the bomb, or should it be calculated from the ultimate analysis? What directions should be given with respect to the degree of comminution of the coal, the method of sampling, etc.? What directions should be given with respect to technical fuel tests and other methods for the determination of calorific value aside from the bomb-calorimeter method?

*Sub-committee VI. Question 7. Uniform Presentation of Analytical Results.* (Pages 226-279.)—The report upon this subject contains a discussion of various methods for expressing the results of analysis, to be used in the following lines of work:

I. For purely scientific analysis.

- (1) The establishment of chemical composition.
- (2) Determination of formulae.
- (3) Gas analysis.
- (4) Inorganic salts and the salts of metals with organic acids.
- (5) Double salts and complex compounds.
- (6) Mixtures, pigments, glass, cement, gunpowder, etc.
- (7) Minerals and rocks.
- (8) Organic substances.

II. Analysis of materials used in the trades and industries.

- (1) Products of the chemical industries.
- (2) Metals, ores and minerals.
- (3) Inorganic and organic dye-stuffs.
- (4) Medicines and pharmaceutical products.
- (5) Foods, beverages, perfumes and photographic materials.

III. Analysis of solutions.

- (1) Natural and artificial mineral waters. \*
- (2) Drinking water.
- (3) Solutions in general.
- (4) Urine analysis.

*Sub-committee VII. Question 10. Determination of Arsenic in Wall-paper, Fabrics, Etc.* (Pages 280-318.)—The report embraces articles upon the following subjects: (1) Electrolytic Method for the Estimation of Arsenic in Wall-paper, Fabrics and Similar Materials, by Chairman T. E. Thorpe; (2) Experiments on the Determination of Small Amounts of Arsenic Acid by Iodometric Acidimetry, by P. Klason and J. Köhler; (3) Quantitative Method for the Determination of Small Amounts of Arsenic in Commercial Articles, by J. Köhler; (4) Report of Estimation of Arsenic in Wall-papers, Tissues, etc., by H. W. Wiley.

(1) This method involves the use of an apparatus already described by the author (*J. Chem. Soc.* **83**, 974 (1903)). A weighed portion of the sample to be analyzed (usually about 2 grams) is treated in a platinum dish first with a little hot water, then with 20 cc. of arsenic-free lime-water and 0.5 gram of calcined magnesia. The material is next heated until the organic matter is thoroughly charred, when the dish is placed in a muffle furnace and heated until the carbon has been burned off. When cold the ash is moistened with water and is treated with 20 cc. of dilute sulphuric acid. After it has been warmed the material is transferred to a flask of about 120 cc. capacity. Half a gram of potassium meta-bisulphite is added, and the solution is boiled until free from sulphurous acid. The solution is now cooled, and is diluted to 50 cc. An aliquot portion is then taken for use in the apparatus. In order to admit of convenient comparison with standard deposits of arsenic, the deposit from the solution under consideration should contain not less than 0.005 mg. nor more than 0.0125 mg. of arsenic. Further details concerning the manipulation of the apparatus and the preparation of the standard deposits are given in the article.

(2) The work upon this subject embraces experiments upon (a) the direct titration of arsenic acid with  $n/2$ KOH; (b and c) the titration of arsenic acid by iodometric acidimetry; (d) the temperature to which small amounts of arsenic acid may be heated without loss; (e) the oxidation of arsenious to arsenic acid; (f) the titration of arsenic acid after distillation of the arsenic as trichloride; (g) the determination of small amounts of arsenic in paper; (h) the determination of arsenic in wool; (i) the stability of very dilute ( $n/1000$  to  $n/500$ ) hyposulphite solutions; (j) the stability of  $n/500$  iodine solution. The principal points of interest in the experiments may be briefly stated as follows: (a) This method was found to give only approximately correct results, (b and c). This method is based upon the addition to the acid of a solution containing 1 equivalent of potassium iodate and 5 equivalents of potassium iodide. The amount of iodine liberated is determined by means of a hyposulphite solution. With proper precautions accurate results were obtained by the authors with a series of solutions containing from 0.067 mg. to 203.01 mg. of arsenic. The method is to be recommended provided organic substances are absent. (d) It was found that small amounts of arsenic acid (0.676 mg.) could not be heated to a temperature above  $100^{\circ}$  for a long time (several hours) without loss, probably due to reduction effected by dust particles in the air. (e) Nitric acid alone will not completely oxidize arsenious to arsenic acid, but will do so in presence of hydrochloric acid. (f) The temperature must be raised rapidly in order to prevent loss of hydrochloric acid before the temperature is reached at which distillation of the arsenic trichloride commences. (i) After ten days the loss

undergone by the  $n/500$  solution was 3.9 per cent.; after seventeen days the loss in the case of the  $n/1000$  solution was 12.7 per cent. (7) After thirty-two days the loss was 1.14 per cent.

(3) In this article is described a series of experiments intended to supplement the work of Klason and Köhler, with a view to eliminating the difficulties arising when organic matter is present. The procedure is essentially as follows. The arsenic is either converted into the trichloride by distillation with hydrochloric acid and then into arsenic acid by nitric acid, or it is precipitated as arsenious sulphide and then oxidized by nitric acid. After it has been evaporated to dryness the arsenic acid is treated with potassium permanganate (2 cc. 5 per cent. solution, with 1 cc. 30 per cent. sulphuric acid) in order to eliminate organic matter. It is then heated over a water-bath ten to fifteen minutes, and is reduced with sulphurous acid (10 cc. 7 per cent. solution). The sulphurous acid is removed by heating for thirty minutes to a temperature of 50–70°, and then to 100°. This treatment is repeated with 5 cc. of sulphurous acid, and the solution is again evaporated until complete removal of the sulphurous acid has been effected. If the liquid is not perfectly clear after the first treatment, oxidation with permanganate should be repeated. The residue is dissolved in 15 cc. of water, is neutralized with sodium bicarbonate, and is titrated with  $n/500$  iodine solution. Starch is added, and the solution is vigorously shaken during the titration. The bicarbonate solution alone requires about 2 drops of the iodine solution before the blue color appears. The color remains but a few seconds. The method has been tested by seven different chemists with satisfactory results.

(4) This article contains a description of the method employed in the Miscellaneous Laboratory of the Bureau of Chemistry for the determination of arsenic in wall papers and fabrics. A full account of this method, which is essentially a modification of the method of Sanger (*Pr. Am. Acad. N. S.* 18, 24 (1891)) has already been published. (Bulletin 86, Bureau of Chem. U. S. Dept. Agr. (1904)). Some use has been made of the electrolytic method of Thorpe (described above) in the Bureau of Chemistry. Most excellent results were obtained.

*Sub-committee VIII. Question 11. Determination of Boric Acid, Benzoic Acid, Salicylic Acid and Other Substances Used in the Preservation of Foods.* (Pages 319–343.)—The report includes two articles (1) by M. L. Lindet, chairman of the sub-committee, and (2) by H. W. Wiley.

(1) A general discussion is given in this article of the methods employed in the determination of the following substances: salicylic acid, benzoic acid, boric acid, borax, fluoborates, fluorides, alkaline fluoborates, alkaline fluosilicates and formaldehyde.

(2) In this paper is given a detailed description of the methods now used in the Bureau of Chemistry for the detection and deter-



mination of the following substances: formaldehyde, sulphurous acid, salicylic acid, saccharin, benzoic acid, boric acid and the borates, fluorides, borofluorides and silicofluorides. An account is also given of the methods used in the detection of coloring-matter in foods, in the determination of annatto in butter or other fat, and in the detection of coloring-matter in milk.

*Sub-committee IX. Question 12. Determination of Sulphur in Pyrites, Blendes, Etc.* (Pages 344-399.)—This report consists in the main of two articles, both of which have already been published elsewhere: (1) Determination of Combined Sulphuric Acid by the Methods of Lunge and of Silberberger, by G. Lunge (*Z. angew. Ch.* **18**, 449 (1905)). (2) On the Determination of Sulphuric Acid by Precipitation with Barium Chloride in Presence of Interfering Substances, by G. Lunge and R. Stierlin (*Z. angew. Chem.* **18**, 1921 (1905)). By referring to the following additional articles (Silberberger, *Ber.* **36**, 2755 (1903); Lunge, *Ibid.* p. 3387; Silberberger, *Ibid.* p. 4259; Lunge, *Z. angew. Ch.* **17**, 913 and 949 (1904); Küster, *Ibid.* p. 1180; Lunge, *Ibid.* p. 1180; Pattinson, *J. Chem. Ind.* **24**, 7 (1905); Hintz and Weber, *Z. anal. Chem.* **45**, 31 (1906); Dennstedt and Hassler, *Z. angew. Ch.* **18**, 1562 (1905); Lunge, *Ibid.* p. 1656; v. Knorre, *J. Chem. Ind.* **28**, 2 (1905)), more complete information concerning the method of Lunge may be obtained. This method is recommended by the ninth sub-committee for international use in the determination of sulphur in pyrites, blendes, etc.

*Sub-committee X. Question 13. Is it Necessary to Calculate the Percentage of Manganese in a Permanganate Solution, the Strength of which with Respect to Iron is Known, by Means of a Coefficient Different from that Indicated by the Equation?* (Pages 400-418.)—As a result of the experimental work performed by himself and his coworkers, chairman L. L. de Koninck draws the conclusion that it is possible, under conditions easily established, to obtain a sharp reaction between potassium permanganate and manganese salts, in the ratio  $3\text{MnCl}_2:2\text{KMnO}_4$ . It is therefore unnecessary to employ an arbitrary coefficient in calculating the strength of a permanganate solution from the analytical results obtained by a suitable modification of the Guyard method. The procedure adopted by de Koninck in proving his contention is essentially as follows: A measured volume of permanganate solution is reduced by heating with hydrochloric acid. The moderately acid manganous solution thus obtained, to which pure ferric chloride has been added, is treated at a slightly elevated temperature with zinc oxide suspended in water, until the point is reached at which further addition of the oxide effects a rather sudden coagulation of the precipitate. The supernatant liquid after it has been shaken (and warmed, if necessary) is completely clear and colorless, or at least only slightly milky. After diluting to about 300 cc. and adding in the majority of cases 20 grams of

zinc sulphate the author titrates the solution at about  $100^{\circ}$  with the permanganate solution (of which a portion was reduced at the outset) until a pink color is obtained which persists even after the solution is boiled. The volume of permanganate solution required was in every case almost exactly two-thirds that of the permanganate solution reduced. This is obviously in accord with the ratio  $3\text{MnCl}_2:2\text{KMnO}_4$ . The author recommends for actual work a procedure somewhat as follows: A sample of manganiferous iron ore (for example) is dissolved in hydrochloric acid; the filtered solution, moderately acid, is diluted to 500 cc. Two samples of 100 cc. each are taken from this solution. To one of these samples is added the manganese chloride obtained by reduction of a measured volume of the permanganate solution with hydrochloric acid. After the iron has been removed from both samples by the addition of zinc oxide, the solutions are titrated with permanganate. From the difference the strength of the permanganate solution may be calculated, while from the lower result may be obtained the percentage of manganese in the sample.

The report upon this question contains also an article by G. Chesneau which has been published elsewhere (*Annales des Mines*, Feb. (1906)). This piece of work contains some experimental evidence corroborating the conclusions of de Koninck.

*Sub-committee XI. Question 14. Methods of Analyzing Materials Containing Tartaric Acid.* (Pages 419-421.)—For the determination of bitartrates it is proposed to abandon the method of direct titration without filtration. The approved method is briefly as follows: In a 500 cc. flask is placed 2.35 grams of the fine material, with 400 cc. of distilled water. The liquid is boiled for five minutes. Water is added, and the liquid is cooled, shaken, and is filtered upon a folded filter-paper. Of the filtrate 250 cc. are boiled in a porcelain dish, and titrated (neutral litmus-paper as indicator) with  $\text{N}/4$  potash that has been standardized under the same conditions with a pure bitartrate. For the analysis of total tartaric acid the method of Goldenberg-Géromont (*Z. anal. Ch.* **37**, 312 (1898)) is usually employed. This method has been studied in detail by the committee. A brief statement is also made concerning the correction to be introduced for the volume of solid material—a subject to be considered in greater detail in a future report.

## RECENT WORK IN AGRICULTURAL CHEMISTRY.

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### FERTILIZERS BY F. P. VEITCH.

As usual, numerous experiments have been made for the purpose of determining the relative value of different materials for supplying the essential elements, phosphoric acid, nitrogen and potash.

Only those which are deemed most important need be mentioned here. Haselhoff (*Landw. Jahrb.* **34**, 616-641 (1905)) has conducted a number of experiments to show the value of differently prepared and different mixtures of Thomas slag. Kuhnert (*Mitt. deut. landw. Ges.* **20**, 334 (1905)) has found slag to give better results during the first year than crude ground phosphate. Clausen (*J. landw.* **53**, 213-228 (1905)) has investigated by pot experiments the effect of phosphoric acid on oat plants grown on black peaty sand and has found the total yield to regularly increase while the relative yield of grain was decreased.

In an investigation of the influence of phosphoric acid on wines from grapes, Zacharewicz (*Prog. agr. int.* (Ed. L' Est) **25**, 459-462 (1904)) finds that phosphoric acid may be accumulated in part in the fruit and contribute beneficially to the wine made from it. Montanari (*Staz. sper. agr. ital.* **38**, 253-258 (1905)), Quartaroli (Abs. in *J. Chem. Soc.* **88**, ii, 549 (1905)), Pervinquier (*Rev. sci.* **5**, [4] 353-361 (1905)), and Katayama (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 353-356 (1905)) have contributed minor papers on phosphoric acid. Haselhoff (*Landw. Jahrb.* **34**, 647-664, pl. 1 (1905)), in extended pot experiments with various potassium fertilizers on potatoes followed by wheat, finds that a partial substitution of potassium chloride by sodium chloride resulted in a slight increase in yield of potatoes but a further increase of sodium chloride gave a decrease in yield. The smallest amount of potash was taken up by potatoes from the kainit. The author concludes that it appears probable that by the application of sodium chloride the potash of a soil is rendered soluble and more easily assimilated by plants.

By treating leucite with various salt solutions, and also with water, Monaca (Abs. in *Centr. agr. Chem.* **34**, 714 (1905)) succeeded in dissolving considerable potash from the finely ground material, such potash being considered assimilable plant food. Reitmair (*Z. landw. Versuchsw. Oesterr.* **8**, 863-944 (1905)) reviews the work of other investigators regarding the conditions under which potash fertilization reduces the protein content of malted barley and concludes that the protein content is only reduced when the quantity of available potash in a soil is at a minimum and is especially reduced on the less fertile soils when a heavy application of nitrogen has been given. Stoklasa (*Z. landw. Versuchsw. Oesterr.* **8**, 957-982 (1905)) presents a reply to the conclusions drawn by Reitmair on this subject. Vageler (*Vrtljschr. bay. landw. rat.* **10**, [2] (Ergänzungsh.), Sup. 1, 125-133 (1905)) has examined 143 cultivated Bavarian moor soils and finds that in spite of the fact that they are well supplied with potash they are much benefitted by a liberal application of potash fertilizers. Feilitzen (*Svenska mosskulturför. tidskr.* **19**, 91-100, pls. 4, Fig. 1 (1905)) finds that mangolds and potatoes grown on moor soils frequently show marked need of potash. Prianišnikov (*Ber.*

*deut. bot. Ges.* **23**, 8-17 (1905)), in reviewing experiments on the effect of ammonium salts on the assimilation of phosphoric acid, concludes that phosphates are rendered more soluble by these salts while sodium nitrate exerts no such effect. Bachmann (*Fühling's landw. Ztg.* **54**, 219-223 (1905)) finds that calcium carbonate applied with sulphate of ammonia increases its action while the action of nitrate of soda is not materially affected by the calcium carbonate. Treboux (*Ber. deut. bot. Ges.* **22**, 570-572 (1904)) has studied the effect of various forms of nitrogen on chlorophyll-bearing plants and finds that nitrites, while generally available in alkaline soils, are poisonous in acid soils. Nitrates and nitrites were found to possess practically the same efficiency while ammonium salts were more available than either. Amines and amides are about equally valuable for the lower plants but amides are less assimilable for the higher chlorophyll-bearing plants. It is claimed that ammonium salts are most suited to the nitrogen nutrition of chlorophyll-bearing plants and that the intervention of nitrite and nitrate bacteria is not always necessary.

The value of calcium cyanamide or lime nitrogen as a nitrogen carrier has received a great deal of attention from European investigators, the following authors contributing to the literature on this subject: Haselhoff (*Landw. Jahrb.* **34**, 597-616 (1905)); von Seelhorst and Muther (Abs. in *J. Chem. Soc.* **90**, ii, 46 (1906)); Immendorff and Thielebein (*Fühling's landw. Ztg.* **54**, 787-795 (1905)); Ashby (*J. agr. sci.* **1**, 358-360 (1905)); Grandeau (*J. agr. Prat.*, N. S., **10**, 808 (1905)); von Feilitzen (*Svenska Mosskulturför. Tidskr.* **19**, 100-110 (1905)); Otto (Abs. in *J. Chem. Soc.* **88**, ii, 196 (1905)); Söderbaum (*Meddel. K. Landtbr. Akad. Exptäfl.* (Stockholm), No. 85, 27), Löhnis (Abs. in *Chem. Centr.* **1**, 1731); Wein (*Chem. Ztg.* **29**, 1066 (1905)); Grandeau (*J. agr. prat.* N. S. II 8-10 (1906)). Without going into the details of these results, it may be said that in general the experiments have shown that the use of this material upon land on which crops are immediately to be planted, may prove decidedly injurious if large quantities of the material are applied but if the application be made some time before planting the crop, little, if any, injury results. As a nitrogen carrier this material promises to be a valuable addition to our fertilizer materials and to have a value about equal to ammonium sulphate, though this value will differ somewhat with the nature of the soil upon which the material is used.

The formation of nitric acid from the air has continued to occupy a prominent place in the experimental and technical fields and Birkeland and Eyde have devised a process that, according to Witt (*J. Chem. Ind.* **28**, 699 (1905)), is exceedingly promising. The inventors, instead of working with arcs of low amperage, utilize the action of a magnetic field on the arc, by placing powerful electromagnets vertically to the electrodes; the arc formed be-

tween the electrodes is blown away, as it were, by the influence of the magnetic field and at once a new arc is formed which is also blown away. In practice, this formation and removal of the arc takes place several hundred times per second. With 30 kilowatts energy, discs of one metre diameter can be formed. The hollow electrodes are of copper and are cooled internally by water. A yield of 100 grams nitric acid per kilowatt hour is obtained at a cost of about 1 to 2 cents per kilo. The dilute acid is concentrated as much as possible by running the oxides into the solution which is then treated with lime water to form a calcium nitrite which is oxidized to nitrate by treatment with nitric acid. The solution is evaporated and fused, resulting in a basic nitrate which powders readily, and in contact with water, soil and carbon dioxide breaks down into calcium carbonate and nitrate. Schloesing (*Compt. rend.* **141**, 745 (1905)) finds calcium nitrate and nitrite as effective fertilizers as the sodium salts for maize. Bellenoux (*Compt. rend.* **140**, 1190 (1905)) finds calcium nitrate fully as valuable as sodium nitrate in the production of potatoes and sugar beets.

Other papers upon the value of various nitrogenous materials have been contributed by Lutz (*Bull. soc. bot. france*, **52**, 159-162 (1905)); Haselhoff (*Landw. Jahrb.* **34**, 642-646 (1905)); Aumann (Abs. in *Centr. agr. Chem.* **33**, 852 (1904)); Bjorn-Anderson (*Tidsskr. Landökonom.* 160-168 (1905)); Knecht (*Chem. News*, **91**, 259-261 (1905)); Clausen (*Deut. landw. Presse*, **32**, 611 (1905)); Gerhardt (*Chem. Ztg.* **29**, 194 (1905)); Schäfer (*Fühling's landw. Ztg.* **54**, 142-145 (1905)); Gerlach and Vogel (Abs. in *Chem. Centr.* **1**, 1609 (1905)); Böhme (*Illus. landw. Ztg.* **24**, 1001, 1011, and 1023-1025 (1904)); Boullanger and Massol (*Compt. rend.* **140**, 687-689 (1905)); Lutz (*Compt. rend.* **140**, 380-382 (1905)); Weitz ("Der Chilisalpeter Düngemittel," Berlin: Paul Parey, (1905)); Müller and Spitzer (*Ber.* **38**, 778-782 (1905)); Jamison ("Utilization of Nitrogen in Air by Plants," Report of the Agricultural Research Association of the N. E. Countries of Scotland (1905)) advances the startling doctrine "That plants generally absorb free nitrogen directly from air, and transform it into albumen, that the quantity absorbed and fixed varies according to the number and character of the special structures that perform such function, and to the presence of the conditions of growth necessary to secure development of such structures." It is further stated that neither fungi nor bacteria have the power of fixing free nitrogen but that this power is limited to chlorophyll-bearing plants, and that the seat of fixation is in certain structures of the leaf or stalk. The evidence upon which these conclusions are based is simply the presence of albuminous material in these above-mentioned structures. It is not likely that Jamison's conclusions will be accepted on the evidence submitted. Fisher (*J. Landw.* **53**, 289-297 (1905)) in studying nitrogen-fixing bacteria

has found that the activity of the organisms is greatly influenced by the character of the soil, particularly by its lime content and physical condition. In one soil where the several plots were differently manured only those to which lime has been applied contained *Azotobacter*. Löhnis (*Centr. Bakt.* **13**, 706-715 (1904); **14**, 582-604 (1905)) has studied the various nitrifying and denitrifying bacteria and concludes that because soil conditions are as a rule more favorable to nitrification than denitrification, the latter is inconsiderable in well aerated soils. Keutner (*Wiss. Meeresunters.*, abt. Keil 8) finds nitrogen-fixing bacteria widely distributed in sea water and in many fresh waters. *A. chroococcum* has the power to fix nitrogen in an 8 per cent. solution of sodium chloride.

The use of lime as an adjunct in agricultural practice is a subject receiving a great deal of attention, and Suzuki (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 347-351 (1905)) finds that calcium carbonate decidedly depresses the assimilability of phosphoric acid by rice while calcium sulphate has no such effect. Powdered magnesite also greatly depresses the yield. Loew (*Z. landw. Versuchsw. Oesterr.* **8**, 583-602 (1905)) and Loew and Aso (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 335-346 (1905)), in investigations upon the ratio of lime to magnesia, find that this ratio is dependent upon equal availability in the forms in which the lime and magnesia exist, and Loew maintains his well-known views regarding the necessity of having a definite relation between lime and magnesia in the soil in order to insure the highest productiveness. Hoffmann (*Arb. deut. landw. Ges.* No. **106** (1905)) reports in detail a large number of experiments conducted under the auspices of the German Agricultural Society in which the use of lime in rotation experiments proved beneficial in a majority of cases. On light poor soil in dry seasons carbonates proved preferable to caustic lime. Methods for applying different forms of lime are given. Meyer (*Fühling's landw. Ztg.* **54**, 261-267 (1905)), having found that crops grown in zinc pots and fertilized with gypsum gave small yields, has repeated his experiments checking the results with earthenware pots and finds that the yield of leguminous crops is much reduced in zinc pots but that the injury was overcome by adding calcium or magnesium carbonate. Tacke (*Fühling's landw. Ztg.* **54**, 331 (1905)), in referring to the above-mentioned work of Meyer's, calls attention to the earlier work of Fleischer and Tacke and Immendorff with gypsum on acid upland moor soils which indicated that the injury was due to the setting free of acids, and claim this is the explanation for Meyer's results. (This same injury has been observed in the work of the Bureau of Chemistry, U. S. Department of Agriculture, and it should be remembered that zinc sulphate which is undoubtedly formed, is of itself a decidedly acid salt and fully capable of producing all the injury observed, if present in sufficient quantity. Careful ex-

amination renders it doubtful that any quantity of free acid results during the reaction. It seems more plausible, therefore, to attribute the injury to the salt rather than to the free acid.—*Reviewer.*) Hardt (*Deut. landw. Presse*, 32, 253–254 (1905)) has published results of four years' culture and liming experiments on moor soils. Sutherst (*Chem. News*, 92, 185 (1905)) proposes to determine the availability of phosphoric acid in 1 per cent. citric acid and finds that the presence of soluble salts modifies considerably the solubility in this reagent. Rippert (*Fühling's landw. Ztg.* 54, 608–620 (1905)) has reviewed the investigations relating to the fertilizing value of different forms of nitrogen, potash and phosphoric acid and points out that in judging of the efficiency of a fertilizer, a number of different factors such as geographical position, climate, amount of precipitation, geological character of the soil, chemical and physical properties, depth of the surface soil as well as the character of the subsoil must be considered.

Notwithstanding the fact that a great deal of work has been done and that the methods at present for the estimation of fertilizer constituents are in a very good shape, a number of investigators have continued to devote considerable time to improvements in methods with a view of shortening the operation or increasing the accuracy of results. Hissink and Van der Waerden (*Abs. Chem. Centr.* 1, 1188 (1905)) have so modified the volumetric determination of phosphoric acid as to secure a uniform composition of the yellow precipitate. Hlavnicka (*Z. angew. Chem.* 18, 655 (1905)) describes a simple modification of Hundeshagen's method, precipitating the magnesium-ammonium phosphate by the citrate method, washing on a hardened filter with 2½ per cent. ammonia and then with alcohol until free from ammonia, the total volume of washing not exceeding 40 cc. The titration is made, using methyl orange as an indicator. Hirt and Steel (*Proc. Soc. Chem. Ind. Victoria* (1905) 14–19, and *Chem. News*, 92, 113–114 (1905)) slightly modify Littmann's method, which they consider preferable to Pemberton's for commercial work. Raschig (*Z. angew. Chem.* 18, 374–376 (1905)) shows that the amount of water used in washing magnesium-ammonium phosphate prior to titration may be reduced to 10 cc. Neubauer (*Landw. Vers. Stat.* 63, 141–149 (1905)) gives a simple method for the determination of phosphoric acid, potash, sodium, calcium and magnesium in hydrochloric acid soil solutions. Schultze (*Chem. Ztg.* 29, 508 (1905)) estimates calcium oxide and phosphoric acid volumetrically and shortens the regular method for the determination of potash as potassium chlorplatinate.

Schenke (*Landw. Vers. Stat.* 62, 3–10 (1905)) makes a comparative examination of Märcker's German official citrate method and a modified citrate method for the determination of phosphoric acid in bone meal, Thomas slag and soils. The results

of the modified citrate method agree most closely with the molybdic method. The author points out that the citrate method is a "compensation method." Mach (*Landw. Vers. Stat.* **63**, 81-91 (1905)) finds that the Wagner method and the official German method for determining phosphoric acid agree closely as a rule. The Wagner method gave higher results in slag rich in silica. The Schenke modification of the citrate method gave results that were too high. Seib (*Z. anal. Chem.* **44**, 397-398 (1905)) offers a substitute for the Petermann method as used in Belgium, which shows results agreeing quite closely with the Petermann method. Ledoux (*Abs. J. Chem. Ind.* **24**, 904 (1905)) detects natural phosphates in phosphatic slags by extracting the phosphoric acid of the mixed phosphates with citric acid. This dissolves the phosphoric acid of the slag. The residue is treated with nitric acid and if on adding ammonium molybdate to the solution a precipitate is formed, the presence of natural phosphates is indicated. Svoboda (*Chem. Ztg.* **29**, 453-456 (1905)) has made a critical examination of the Maercker-Buhring solution, Wagner's citrate magnesia mixture, and iron citrate magnesia mixture to show their solvent effect on glass. Boulez (*Internat. Kong. angew. Chem. Ber.* **3**, 746-747 (1903)) determines phosphoric acid in the presence of other constituents in phosphatic material by titrating with alkali, using methyl orange and phenolphthalein as indicators.

Jarvinen (*Z. anal. Chem.* **44**, 333-342 (1905)) determines magnesium in a solution exactly neutralized, using lacmoid as indicator, by the cautious addition of a slightly ammoniacal solution of diammonium phosphate. After standing a short time, 1 per cent. ammonia is added and then 10 per cent. ammonia in quantity equal to one-third the volume of the whole. The determination is made after two hours' standing. Baxter and Griffin (*Am. Ch. J.* **34**, 204-217 (1905)) find that the precipitate of ammonium phosphomolybdate occludes a small amount of molybdic acid which renders the results by this method slightly inaccurate. It is also claimed that 24 molecules of alkali are required for the neutralization of one molecule of ammonium phosphomolybdate and not 23 as commonly assumed. The authors conclude that no method for estimating phosphoric acid which depends upon the determination of the molybdic acid in ammonium phosphomolybdate is accurate unless allowance is made for the occluded ammonium molybdate and molybdic acid. Gerhardt (*Chem. Ztg.* **29**, 178-179 (1905)) determines free phosphoric acid in superphosphates by shaking 20 grams of the superphosphate mixed with 1 gram of ferrocyanide of potassium dissolved in a little water for one-half hour in a liter of water. Filter, add a known weight of calcium carbonate to 100 cc. of the solution and stir for one-half hour. Remove the excess of calcium carbonate by filtering, wash, dry, burn, ignite carefully and weigh.



The difference between the calcium carbonate used and that thus obtained furnishes a means of determining free phosphoric acid. Zöckler (*Chem. Ztg.* **29**, 226-338 (1905)) believes that Gerhardt's method is unreliable and considers the alcohol method safer. Ostersetzer (*Chem. News*, **91**, 215 (1905)) briefly describes the method for using alizarinsulphonic acid as indicator in determining free acid in superphosphates.

Westhausser (*Z. anal. Chem.* **44**, 187-191 (1905)) compares the official German method, the original Kellner-Böttcher method and the Kellner-Böttcher method, using Hallens ammonium citrate solution. All were unreliable on Thomas slags containing large amounts of silica. Alvarez (*Chem. News*, **91**, 146 (1905)) proposes to use sodium aminonaphtholsulphonate for the precipitation of potash in neutral solutions. The precipitate may be washed in alcohol. Ammonium and magnesium salts do not interfere with the reaction. Klinkerfues (*Chem. Ztg.* **29**, 77-78 (1905)) estimates potash by direct evaporation of the water solution with chlorplatinic acid and, after washing the potassium chlorplatinate with a very little water and with alcohol, dissolves it in water in a platinum dish and precipitates metallic platinum by decomposing the salt with formic acid. In a later communication (*Chem. Ztg.* **29**, 1085-1086 (1905)) the author states that it is not necessary to completely dry the salt after the addition of formic acid. This, however, greatly shortens the operation. Pfyl (Abs. in *Analyst*, **30**, 345-346 (1905)) determines nitric acid in the presence of organic substances by reducing nitric acid to nitric oxide by means of ferrous chloride and hydrochloric acid, the nitric acid being washed by passing it through sodium hydroxide solution and absorbing by tenth-normal potassium permanganate solution. The excess of permanganate solution is titrated with tenth-normal ferrous chloride solution. Frerichs (Abs. in *Chem. Centr.* **1**, 957 (1905)) calls attention to the fact that the reaction between nitric acid and diphenylamine is interfered with by the presence of such substances as ferric salts, chromates, etc., and proposes to obviate some of the difficulty by treatment with ether in sulphurous acid solution. Gutbier (*Z. angew. Chem.* **18**, 494-499 (1905)) reports tests of the accuracy of Busch's method for the determination of nitric acid. The Busch method (*Ber.* **38**, 861-866 (1905)) is based on the fact that diphenyleneanilodihydrotriazol forms insoluble compounds with nitric acid and makes it possible to detect this acid in dilutions of 1:60,000 at room temperature, and 1:80,000 at zero temperature. A list of other substances forming similar precipitates which may interfere is given. Tests on pure potassium nitrate show a close agreement with standard methods.

Meisenheimer and Heim (*Ber.* **38**, 3834-3837 (1905)) describe a method for the determination of nitric and nitrous acids based upon the measurement of the nitric oxide set free when nitrous acid

is treated with hydrogen iodide and when nitric acid is treated with ferrous chloride and hydrochloric acid in the usual way. Raschig (*Ber.* **38**, 3911-3914 (1905)) claims priority for the above method. Bensemann (*Z. angew. Chem.* **18**, 939 and 1225-1228 (1905)) proposes a method for the complete analysis of sodium nitrate. Easton (*Chem. Eng.* **1**, 142-145) estimates nitric acid and nitrates by electrolytically reducing to ammonia in a copper solution acidified with sulphuric acid and distilling the ammonia thus formed.

Schloesing (*Compt. rend.* **141**, 745-746 (1905)) has compared the value of calcium nitrate prepared electrolytically with sodium nitrate and a mixture of sodium nitrite and calcium nitrite for the production of corn in pot experiments. All the substances were equally valuable in increasing the yield. Thiele (*Mitt. landw. Inst. Breslau* **3**, 157-178 (1905)) thoroughly reviews the literature relating to the sampling of soils with particular reference to the difficulty of securing representative samples, showing the small differences occurring in plant-food constituents, particularly nitrogen. The results indicate that it is not possible to get a strictly representative sample by present methods of sampling but that it is possible to detect by analysis smaller variations in nitrogen content than are likely to be of significance in experimental work. Trillat and Turchet (*Bull. soc. chim.* [3] **33**, 308-310 (1905)) have examined the nitrogen iodide reaction for determining ammonia in potable waters. They also (*Ibid.* pp. 304-308) propose a new method for determining ammonia which is based upon the fact that when 3 drops of a 10 per cent. potassium iodide solution and 2 drops of a saturated alkali hypochlorite solution are added to 20 or 30 cc. of water containing ammonia, a black coloration is formed. Flamand and Prager (*Ber.* **38**, 559-560 (1905)) modify Kjeldahl's method to make it applicable for the determination of nitrogen in azo-, azoxy-, and hydrazo-compounds. Tschernobajeff (*Chem. Ztg.* **29**, 442-443 (1905)) recommends that chlorates and perchlorates be determined together in sodium nitrate by Lemaitre's method and that chlorates be determined separately by reduction in the cold by means of iron and sulphuric acid according to Hendrixson's method. Bensemann (*Z. angew. Chem.* **18**, 816 (1905)) proposes to reduce nitrate of soda by fusion with oxalic acid until carbonate is formed, and nitrogen and chlorine are expelled.

#### SOILS BY F. P. VEITCH.

The chemical investigation of soils has continued to receive its full share of attention, and a number of workers have endeavored to establish a relation between crop production and the plant food constituents removed from the soil by various solvents. Marr (*Meded. Proefstat. Oost-Java* [4] No. 4, 65-87) finds that many soils of Java, although containing a low percentage of total

phosphoric acid (less than 0.1), yet produce excellent crops and fail to respond to applications of phosphates. Examination of such soils by the methods of Schloesing and of Dyer (using 2 per cent. citric acid) showed that the former method did not give results agreeing with the crop history of the soil, but that the Dyer method showed the soils to contain sufficient assimilable phosphoric acid. Kudasher (*Zhur. Opintn. Agron.* 6, 436-437 (1905)) finds in the examination of 62 samples of Chernozem soils that the most fertile soils yield the most phosphoric acid to 0.5 per cent. oxalic acid solution. Ingle (*J. Chem. Soc.* 87, 43-55 (1905)), from numerous pot experiments with barley, turnips and horse beans, draws the conclusion that while Dyer's 1 per cent. citric acid method measures the relative available plant food in soils at a given time, it does not necessarily show the relative fertility of the soils, as the rapidity with which the available plant food is renewed may differ with the soil. For comparing soils subjected to the same climatic conditions the author deems the method valuable, but does not think that soils from tropical climates may be judged by the standards of temperate climates. This latter thought is also advanced by Couturier (*Bull. assoc. chim. suc. distill.* 22, 1302-1304 (1905)). Hubert (*Monit. sci.* [4] 19, 582-588 (1905)) discusses the value of, and gives methods for the chemical determination of the fertilizer requirements of soil with particular reference to vineyard purposes, and König (*Landw. Vers. Stat.* 61, 371-396 (1905)) critically discusses the determination of productiveness and plant food requirements of soils from the physical and chemical standpoints. Yegorovo (*Zhur. Opintn. Agron.* 6, 315-324 (1905)) finds that a 100 volt current of low amperage passed through the soil greatly increases the solubility of phosphoric acid and of ammonia but lowers that of nitric nitrogen.

Methods for the bacteriological examination of soils have received attention at the hands of Löhnis (*Centr. Bakt.* 2<sup>te</sup> Abt., 14, 1-9 (1905)) and of Remy (*Fi th Internat. Kong. angew. Chem.* 784-794 (1903)). Fabricius and von Feilitzen (*Svenska Mosskulturför. Tidskr.* 19, 84-90 (1905)) find that white moor soils in their natural condition contain but few bacteria, owing to their acid reaction. The bacterial flora is but little changed by drainage but is greatly increased by liming, manuring, admixture of sand and mechanical treatment, and the number of bacteria in a soil is closely related to the temperature, and rises and falls with the latter. It is a well-known fact that soils rich in organic matter are as a rule deficient in available potash, and usually respond readily to applications of potash manures. Recent investigations by Berthelot (*Compt. rend.* 141, 433-445 (1905)) show that humus materials treated with solutions of potassium or calcium salts form insoluble salts of these metals, thus rendering them of no value to plants. Minssen (*Landw. Vers. Stat.* 62, 445-476 (1905)) reviews the literature on diffusion in acid and neutral media,

with particular reference to the effect of humus soils. The author concludes from the literature and his own work that no acids in dilute solutions interfere with the diffusion of water or salt solutions [a conclusion diametrically opposed to that which would be drawn from field or pot experiments with lime on acid clay or humus soils. The influence of lime in increasing the permeability of such soils is too well-known to require discussion, and it would seem that the investigator has missed the point of his work.—*Reviewer*].

Of late years the uses to which peat may be put have increased so rapidly that a discussion of the whole subject is opportunely given by Kerr ("Peat and Its Products," Begg, Kennedy and Elden, Glasgow, 1905). Half a century ago the subject of the absorptive power of soils was quite thoroughly investigated. Recently more work has been done along this line by Dittrich (*Z. anorg. Chem.* **47**, 15-162 (1905)), Dusserre (*Chron. agr. vaud.* **18**, 463-466 (1905)) and by Einecke (*Mitt. landw. Inst. Breslau.* **3**, 299-310 (1905)) without developing anything particularly new. It is desirable that attention should be redirected to this line of work as from a more thorough and general knowledge of the subject the behavior and effects of fertilizers may be more fully understood. Dittrich's results showing that calcium chloride solutions exert more solvent effect on potash, lime and soda than ammonium chloride or acetic acid solutions are worthy of mention. The water requirements of plants have continued to receive attention at the hands of von Seelhorst and Muther (*J. landw.* **53**, 239-259 (1905)) who experimented with oats, clover and bare fallow, using pots sunk to the level of the ground, and found that, where the ground was kept cultivated, 256.7 grams of water produced 1 gram of dry matter in oats, while 270.2 grams of water were required on rolled ground. One gram of clover required 423 grams for the first cutting and 1,124 grams of water for the second cutting. It was found that the loss of nitrogen through drainage was greatest under bare fallow. Murinov (*Mater. Izuchen. Russ. Pochv.* No. 16 (1905)) has attempted to determine the effect of the action of earthworms on the chemical composition of the soils, and finds the solubility of phosphoric acid in 10 per cent. hydrochloric acid is increased in all cases, while the quantity of lime gradually increased in the lower layers of the soil and nitrogen was more evenly distributed than at the beginning of the experiment. Stoklasa and Ernest (*Centr. Bakt.* **2<sup>te</sup> Abt.**, **14**, 723-736 (1905)) finds that enormous quantities of carbon dioxide, about 130 kilos per hectare per day, during the growing season are set free in the soil chiefly through the action of microorganisms and the roots of higher plants, the former producing slightly the most. The authors are of the opinion that this carbon dioxide converts much plant food into soluble forms,

and that the solvent effect of roots is due to the production of carbon dioxide rather than to the secretion of organic acids.

One of the most valuable, if not the most valuable, contribution to the literature of soils and fertilizers of the year is that of Hall ("The Book of the Rothamsted Experiments," John Murray, London, 1905) who summarizes in a clear and practical way the results of various lines of experiments conducted at Rothamsted for more than half a century. Perhaps the most interesting features, because never brought out before in the papers from Rothamsted, are those tables which bring out the effect of fertilizer residues not only on the yield of crops, but also on the physical condition and chemical reaction of the soil, and also upon the nature of the herbage, the action of bacteria, and the loss of beneficial lime salts in drainage waters. The factors which influence the growth of plants in pots have received attention from Lemmermann (*J. landw.* **53**, 173 (1905)) and also from Voelcker (*Ann. Rep. Chem. Soc. London* **2**, 250-251 (1905)) who think that pot experiments should be conducted in triplicate and repeated before accepting them. Lack of agreement between pot and field experiments is attributed to failure to reproduce in pots actual field conditions.

Geological, mineralogical and chemical investigations of soils have been made by numerous workers to which but mere reference can be made here: "Geological Observations on Analyses of Some West Prussian Soils," by Jentzsch (*Landw. Jahrb.* **34**, 165-176 (1905)); "The Composition of West Prussian Soils," by Schmoeger (*Landw. Jahrb.* **34**, 145-164 (1905)); "Geological Notes on Cocoa Soils," by Cunningham—Craig (*Trinidad Bot. Dept. Bull. Misc. Inform.* 196-200 (1905)); "The Mineralogical Analysis of Soils," by Dumont (*Compt. rend.* **140**, 1111-1113 (1905)); "Classification and Nomenclature of Soils According to Mineralogical Constitution," by Lagatu (*Compt. rend.* **141**, 363-366 (1905)); "Contributions to the Chemical Study of Soils, Waters and Mineral Products of the Region of Chari and Lake Tchad," by Hebert (*Compt. rend.* **140**, 163-165 (1905)); "Soil Investigations in the Philippines," by Sanchez (*Bur. Agr. Rept.* 63-76 (1904)); "Study of Belgian Soils," (*Bull. Agr.* (Brussels) **2**, 85-121 (1905)); "Some Soil Analyses," by Pardy (*Natal. Agr. J. Min. Rec.* **18**, 573-574 (1905)); "Analysis of Spanish Soils" (*Abonos Químicos.* **5**, 25-27 (1905)); "Soils of the Argentine Republic," by Cravetti and by Huergo (*Am. Min. Agr. Argentina, Sec. Agr. (Agron)* **1**, 12-59 and 21-65 (1905)); "Soils," by Ingle (*Transvaal Agr. J.* **3**, 731 (1905)); "The Sugar Soils of Jamaica," by Cousins (*Bull. Dept. Agr. Jamaica* **3**, 137-146 (1905)); "The Soils of Montserrat," by Watts and Tempany (*West Indian Bull.* **6**, 263-284 (1905)).

The value of mechanical analysis of soils is considered by Atterberg (*Chem. Ztg.* **29**, 195-198 (1905)), who proposes a new

classification of the different grades of soil particles, and also by Mitscherlich (*Fühling's landw. Ztg.* **54**, 673-675 (1905)) who, while believing that the determination of hygroscopic moisture and of heat evolved on moistening is of no importance from the standpoint of plant growth, thinks that for judging the character of soils mechanical analysis may be replaced by the determination of the heat evolved on moistening or preferably by determining hygroscopicity. Sjollem (J. *landw.* **53**, 67-69, 70-76 (1905)) proposes to isolate colloidal substances by centrifuging the soil and noting the behavior of the colloids with coloring-matters. The value of the determination of loss on ignition is seriously questioned by Mehring (J. *landw.* **53**, 229-257 (1905)), who thinks that the errors of this determination are increased by attempting to restore carbonates by treating with ammonium carbonate. It is claimed that the direct determination of humus by combustion with copper oxide or chromic acid is more reliable and useful than incineration. A number of articles dealing with the estimation of certain soil constituents have appeared during the year, among which may be mentioned papers by Pellet and Tribourg (*Ann. chim. anal.* **10**, 413-416 (1905)); Schultze (Z. *landw. Versuchs. Oesterr.* **8**, 70-72 (1905)); Amos (J. *Agr. Sci.* **1**, 322-326 (1905)); Wohltmann and Schneider (Chem. *Ztg.* **29**, 810-811 (1905)); Sommer (Deut. *landw. Presse*, **32**, 692 (1905)).

#### WATER BY W. W. SKINNER.

In the examination of mineral waters the phenomenon of radioactivity has attracted much attention. Blanc (*Phil. Mag.* **9**, 148-149) examined numerous samples from Alpine regions and found that most of them produced a certain amount of emanation. In some cases the rate of decay was approximately equal to that of the radium emanation. Some of the deposits, however, produced very little or else a very rapidly decaying emanation, from which the author concludes that the latter are probably due to thorium. The Wiesbaden Thermal Springs were examined by F. Henrich (*Monatsh.* **26**, 149-184) and found to be radioactive. The gases obtained by boiling the waters were radioactive, which phenomenon was much intensified by the removal of the carbon dioxide. The evaporated residue consisting mostly of sodium chloride was found to be only slightly radioactive, but calcium carbonate in the form of aragonite which is deposited from the water at some distance from the spring was found to be strongly radioactive. Mache and Meyer (*Monatsh.* **26**, 595-625) examined some of the mineral springs of Bohemia including Karlsbad, Marienbad and Franzenbad, and found them radioactive. They also found that the rate of decay was about the same as that of radium emanation. The presence of thorium could not be detected. In Karlsbad it was

found that the cold ferruginous spring situated within the thermal belt contained a greater proportion of radium emanation than any of the hot springs. The waters from the St. Joachimsthal mines were also found to be radioactive, and the activity increased with the depth of the source. The lowest spring was found to contain a larger proportion of radioactive emanation than any water heretofore examined. The Gastein Thermal Springs were examined by Mache (*Monatsh.* 26, 349-372) and found to be radioactive with a rate of decay approximately equal to that of the radium emanation. The active substance was found to be the reissacherite of the deposits from the thermal springs. This mineral nearly equals uranyl nitrate in activity, and contains barium, strontium and calcium, but no uranium. Upon separation the radioactive substance is found along with barium and is presumably radium.

Brown (*J. Chem. Soc.* 87, 1051) reviews critically the Frankland combustion method, the Wanklyn albuminoid ammonia process and the Tidy permanganate method, pointing out the advantages and disadvantages of each. He believes that neither the Wanklyn nor the oxidation method alone, gives any idea of the source of the organic matter. To correct this he suggests a method by combining the Frankland and Wanklyn methods and by so doing obtains the whole of the carbon and nitrogen of the organic matter, in the form of carbon dioxide and ammonia, determining the quantity of each. The author presents considerable data to substantiate his claims for the method, from which he concludes that the new method is as precise as Kjeldahl's and is more applicable to water, requiring a smaller sample, eliminating the use of sulphuric acid and avoiding all bumping in glass vessels. It also requires less time and attention without sacrificing accuracy.

According to Effront (*Chem. Centr.* 2, 1253) on the addition of a definite quantity of bleaching-powder, which has been accurately titrated, to a given volume of water, the loss in active chlorine is a measure of the nitrogen of the ammonia and proteids. The diphenylamine reaction for the detection of nitric acid in waters is proposed by G. Frerichs (*Arch. Pharm.* 243, 80). It is claimed that ferric salts, chromates, etc., do not interfere with the reaction. Franz Utz (*Chem. Ztg.* 29, 177) proposes an improvement upon the above method of Frerichs by evaporation with hydrochloric acid, claiming that with this modification the method gives results favorably comparable with the methods of Schulze-Tiemann and Mayrhofer. A method for the detection of nitrous and nitric acids by means of diphenylamine is also proposed by Raikow (*Chem. Centr.* 1, 402). The estimation of ammonia by the method of Trillat and Turchel is claimed by Cavalier (*Bull. soc. chim.* 33, 745) to be worthless for quantitative work. He believes the method can

be used only after considerable concentration, and even then the nature of the precipitate renders the estimation very difficult. F. Dienert (*Ann. inst. Pasteur*, 19, 541) discusses various methods and describes in detail a method based upon electric conductivity, which it is claimed is well suited to the study of variations of underground waters. A modification of the Winkler method for determining oxygen in water is proposed by Noll (*Z. angew. Chem.* 28, 1767) by which more accurate results may be obtained. The purification of water by means of barium carbonate is proposed by Basch (*Chem. Ztg.* 29, 721). The advantages which are claimed for this procedure are that the permanent and temporary hardness are removed, as well as all the sulphates. This is not the case when caustic lime and sodium carbonate are used for this purpose, one of the results of the latter metathesis being the formation of sodium sulphate which is objectionable for a number of reasons. Calcium peroxide has been proposed by Freyssinge and Roche (*Rev. internat. falsif.* 28, 49) for the sterilization and purification of drinking-water. It is stated that water can be completely sterilized in about two hours by the addition of 0.4 gram of calcium peroxide per liter.

#### FEEDING STUFFS BY W. W. SKINNER.

In the proximate analysis of feeding stuffs the attention of investigators is constantly being directed towards that class of substances coming under the caption of nitrogen-free extract, in an effort to more definitely determine the several components of this subdivision. The method of Ellett (Inaug. Diss. Univ. Göttingen 1904) for the quantitative estimation of pentosans and methylpentosans is an instance of this effort. The method proposed is a simultaneous determination of methylpentosans and pentosans in vegetable products. He confirms Votocek's statement that methylfurfural phloroglucide, even when dried, is soluble in alcohol, while furfural phloroglucide is not. Upon this fact he bases his method by obtaining the two together and weighing, and then dissolving out with alcohol the methylfurfural phloroglucide and again weighing. Details of the method are given and the data offered indicate that the method, as worked out, gives satisfactory results. V. Storch (*Ber. Vet. Land. Lab. Landökonom.* 58, 180) explains in detail the methods employed in the analysis of feeding stuffs by the chemical department of the Copenhagen Experiment Station. The faults of the conventional methods for determining nitrogenous components, crude fiber, and nitrogen-free extract are pointed out and discussed. The author recommends that the following determinations be made, *viz.*, fat, albuminoids, sugar, starch, pentosans, ash, and water, with cellulose and other undeterminable substances grouped by difference. This scheme is now employed at the Copenhagen Station. J. König (*Internat. Kong. angew. Chem.*



5, 1052) describes his method for the determination of crude fiber in foods and feeding stuffs by means of a mixture of glycerol and sulphuric acid. The amount of lignin in the crude fiber is determined by hydrogen peroxide and ammonia, which dissolves the lignin, leaving the pure cellulose. An exhaustive study of the value of sorghum seed as a feeding stuff has been made by Tangl, Weiser and Zartschek (*Landw. Jahrb.* 34, 3-64). The authors experimented with horses, steers, cows, sheep, pigs and poultry, and in addition to studying the digestibility of the seed, the income and outgo of nitrogen were determined. From their work they consider sorghum seed a valuable feed, but that to attain the best results it should be mixed with some other grain. Especially is this true for horses.

#### CEREALS BY J. S. CHAMBERLAIN.

One of the important contributions of the year to the chemistry of cereals is the monograph by F. F. Bruyning, Jr., ("La valeur boulangere du froment," Archives Teyler [II], 9, Parts 3-4, Haarlem (1905)) on the baking value of wheat. It is a book of 217 pages and its object is to give a view of the actual state of our knowledge of the baking properties of different kinds of wheat, especially from the point of view of the milling and baking industries of Holland. E. Fleurent has published under different titles (*Ann. chim. anal.* 10, 129, 195, 238, 276 and 309 (1905), (*Compt. rend.* 140, 99 (1905)) a resumé of his work for several years on the determination of gluten. He draws the following conclusions: (1) Wheat gluten is a definite substance and its mechanical extraction, if carried out under proper conditions, is definite and exact. (2) Distilled water and water containing calcium chloride or sulphate or sodium chloride cause a loss in the determination of gluten, but this loss is lessened if calcium bicarbonate is present. (3) In determining gluten only the soluble proteids are lost in the washing and not the gluten. If calcium chloride or sulphate is present in the wash-water the amount of gluten lost is proportional to the amount of globulin present. (4) Prolonged washing causes a loss in gluten and the gluten so lost always contains gliadin and glutenin in the proportion of 75:25. (5) The acidity of old flours tends to lessen the ease of washing out the gluten but neutralization of the excess acidity by means of sodium bicarbonate makes the determination satisfactory. (6) Allowing the mixed dough to stand before washing tends to loss of gluten. (7) The amounts of gluten extracted at temperatures between 15° C. and 35° C. are practically the same. (8) Water at 16° C. containing 80-90 mg. of salts per liter, of which 80-90 per cent. is in the form of calcium bicarbonate, is the best for washing out gluten. The washing should take ten to eleven minutes and the final washing two to three minutes. The gluten should be dried at 105° C. Results should

agree within 0.20 per cent. The influence of the constituents of brown or low-grade flour on the determination of gluten has been examined by Lindet and Amman (*Compt. rend.* **141**, 56 (1905)) who find that among other things there is present in dark flour a mucilaginous substance which prevents the gluten from adhering together as usual. A determination of the hydrolytic cleavage products of the protein "gliadin" by means of dilute acid has been made by E. Abderhalden and F. Sammely (*Z. physiol. Chem.* **44**, 276 (1905)). They find, as did Osborne and Harris (*Am. J. Physiol.* **13**, 35 (1905)) by practically the same method, that by far the greatest part of the cleavage products obtained is in the form of glutamic acid. They find 31.5 per cent. of glutamic acid while Osborne and Harris found 37 per cent. Also that gliadin yields none of the diamino acid lysine and therefore differs sharply from the alcohol-insoluble protein gluten casein (glutenin) which yields a considerable quantity. The amino compounds obtained as cleavage products of gliadin are as follows: Glycocoll, 0.68 per cent., alanine, 2.66 per cent.; aminovaleric acid, 0.33 per cent.; *a*-proline, 2.40 per cent.; leucine 6.00 per cent.; glutamic acid, 27.60 per cent.; aspartic acid, 1.24 per cent.; phenylalanine, 2.60 per cent.; serine, 0.12 per cent.; tyrosine, 2.37 per cent.; tryptophane, 1.00 per cent.

Chapus (*Bull. Agr. Algerie et Tunis*, No. 7, 11 (1905)) discusses the views held and advanced especially by Fleurent and Balland in regard to the differences in composition between hard wheats and soft wheats, the relation of protein content to yield, the determination of gluten and the significance of the proteins gliadin and glutenin. Physiological experiments with man and the nutritive value of different kinds of flour have been made by P. Fauvel (*Compt. rend.* **140**, 1424 (1905)), who finds, from results obtained using white flour, whole wheat flour and brown army flour, that whole wheat bread, though containing more than twice as much phosphoric acid as the army bread, yet does not yield as much assimilable phosphoric acid as the latter. The whole wheat bread diminished the excretion of urea and produced an appreciable quantity of purine bodies. It also irritated the intestines and diminished the assimilation of other nutrients. The army bread was superior to the white and possessed none of the undesirable properties of the whole wheat bread. A case of poisonous flour made from rye infested with a fungus, *Fusarium roseum*, was reported by A. Yachevski (*Russ. J. exp. landw.* **6**, 249 (1905)).

Work on barley and malt has been carried on by several investigators. Vanha, Kyas and Bukovansky (*Ztg. landw. Versuchsw. Oesterr.* 667 (1905)) have demonstrated that seed of high nitrogen-free extract, low total protein and high soluble protein content gave a crop of increased total yield, an increase in yield of grain, number and weight of stalks and total weight of heads. This

influence is explained by the fact that the nitrogen-free extract acts as reserve material and that the best developed embryo is found in seed of high nitrogen-free extract. They conclude that neither nitrogen-free extract nor protein content are transmitted characters but depend chiefly on the quality of soil and the supply of plant food. Other investigations on the relation between protein content and yield have been made by Schneidewind (*Wochenschr. Brau.* 22, 29 (1905)), who maintains that with barley as with other plants the higher the yield under like conditions the lower the protein content. He claims that this is explained by the fact that in the first and middle period of growth large amounts of nitrogen are assimilated and if growth is then suddenly checked the formation of starch is hindered and the nitrogen content will be high. The bettering of the quality of barley by a mechanical and chemical study of the composition of barley soils has been undertaken by J. Stoklasa (*Chem. Centr.* 1905, I, 761). According to the author the rôle of potash in starch formation is such that the amount of potash assimilated stands in a constant ratio to the amount of starch in the grain. One gram assimilated potash produces 23 to 25 grams of starch. The best brewing barleys and their relation to crop rotation and fertilizers have been investigated by E. Schribeaux (*Ann. brass. dist.* 8, 185 (1905)), and the abnormal character of the barley of the crop of 1904 and beer produced from it has been studied by W. Windisch (*Wochenschr. Brau.* 22, 373 (1905)). The turbidity of the "White" beers obtained may be due either to abnormal albuminoid bodies or to abnormal carbohydrates such as pectins. If due to albuminoid bodies they must be compounds intermediate between albumins and albumoses.

A modification of Lindet's method for the examination of malt has been published by Ford and Guthrie (*J. Inst. Brew.* (London) 11, 206 and 326 (1905)). A study of methods for the ash determination of malt has been made by W. Windisch (*Wochenschr. Brau.* 22, 17 (1905)). The enzymes of malt have been investigated by W. Issajew (*Z. physiol. Chem.* 45, 331 (1905)), who concludes that there is present in barley and malt a substance possessing all the properties of an oxydase. The ease with which it accelerates oxidation, its relation to temperature and toward reagents, its "Spezifität," etc., all serve to show its enzymic nature. Its rôle in various physiological processes, especially in germination, is doubtless very important. J. Effront (*Compt. rend.* 141, 626 (1905)) finds that during germination of malt the saccharifying power and the liquefying power of diastase are developed unequally. The saccharifying power increases irregularly and after having attained its maximum diminishes gradually. The development of the liquefying power is slower but more regular and on reaching its maximum it is maintained for some time. When germination is produced in sunlight the difference in the develop-

ment of the two powers is very marked. These phenomena evidently have a direct relation to the transient formation of acid amides during germination. The action of chemical agents on the germination of barley is very complex. Phosphates, lime water and copper sulphate favor germination. Xylene acts favorably toward both saccharifying power and liquefying power. Ammonium chloride increases the liquefying power. Lactic acid, vegetable peptone and neutral calcium hypochlorite increase germination and both enzymic activities but if the calcium hypochlorite is alkaline, it favors germination but weakens the diastatic power.

A study of the value of different sized kernels of rye for baking and feeding purposes has been made by Bastecky (*Chem. Centr.* 1905, I, 465). The influence of soil moisture on the composition of oats has been investigated by Seelhorst and Fresenius (*J. Landw.* 53, 21 (1905)). Their conclusions from pot experiments are: Straw grown on dry soil is characterized by a high digestible protein content. The albuminoid nitrogen diminishes less with increasing moisture content of soil than do the total nitrogenous bodies. The digestible protein diminishes more rapidly than the total protein. The increase in ash and organic matter during the growth of oats has been examined by M'lle Stefanowska (*Compt. rend.* 140, 58 (1905)). The curves representing the increase in fresh substance, dry substance and ash all have a similar character, increasing slowly per day of growth at first and during maturity increasing very rapidly. The same is true of organic nitrogen, phosphoric acid, lime, potash and iron. An important contribution to our knowledge of the chemical composition and nutritive value of sorghum seed and oats is that by F. Tangl, of the Experiment Station for Animal Physiology of Budapest, and his associates (*Landw. Jahrb.* [3] 34, 65 (1905)). The coefficients of digestibility of sorghum on steers, sheep, horses and swine, and of oats on horses and sheep are given for each constituent. The average composition and nutritive value of both feeds are also given in numerous tables. They calculate the physiological nutritive value of oats fed to horses as 54.80 per cent., with sheep 53.85 per cent. Sorghum grain alone is not a satisfactory feed for horses, but if fed with twice its weight of oats, it is good. Becquerel (*Compt. rend.* 140, 1652 (1905)) has shown that the effect of low temperature upon the vitality of various leguminous and cereal seeds depends upon the amount of water and gas present in the seeds. As the result of experimental work Dumont (*Compt. rend.* 141, 686 (1905)) concludes that the rays of light which act the most effectively upon the migration of albuminoids in grain are those which have the least effect on the chlorophyll function, viz., dark brown, green, blue, red, in the order given. The aleurone grains found in cereals and other seeds have been studied by S. Posternak (*Compt. rend.* 140, 322 (1905)). The aleurone

grains are formed during the maturity of the seed when the kernel is drying out. The common conception that the aleurone grains are reserve nitrogenous material of the seed is not in accord with the facts. About 50 to 75 per cent. of the aleurone grains are proteid material, but the 25 to 50 per cent. of the non-proteid materials play an important part in the life of the embryo plant. The author finds a new organic phosphorus compound, *viz.*, anhydrooxymethylene diphosphoric acid or "phytin" and also an organic acid yielding a reducing sugar by hydrolysis. An elementary analysis of aleurone grains from various seeds shows that they contain a considerable quantity of all those mineral elements considered indispensable to the development of a plant. The author claims, therefore, that the aleurone grains are not simply a source of reserve nitrogenous material, but that they are a complete mineral food for the embryo plant, and that the mineral elements are present in the seed, as in the case of phosphorus cited above, in organic combination.

For the detection of sawdust in flour Paganini (*Chem. Ztg. Rep.* 23 (1905)) recommends the addition, to a thin layer of the flour, of a few drops of a 20 per cent. aqueous solution of phenylendiamine followed by a few drops of acetic acid. A bright yellowish red color is formed in the presence of sawdust. The reagent is claimed to be much more delicate than phloroglucin and hydrochloric acid. In the examination of noodles and other edible pastes, Filsinger (*Z. öffentl. Chem.* 11, 332) and Lührig (*Z. Nahr.-Genuss.* 10, 153 (1905)) suggest the determination of lecithin. Phosphoric acid does not afford sufficient data for judging of the nutritive value of noodles. A fairly complete proximate analysis is suggested as well as the determination of digestibility.

#### FOODS BY W. D. BIGELOW.

*Spices, Etc.*—Jaeger (*Z. Unters. Nahr.-Genuss.* 10, 761-762 (1905)) has discussed at considerable length methods for the detection of cocoa shells in spices. The literature of the subject is reviewed. The presence of reducing sugar in mace has afforded the opportunity, which has not been neglected, of adulterating the product with sugar. Ludwig and Haupt (*Z. Unter. Nahr.-Genuss.* 9, 200-204 (1905)) examined a series of samples of mace and found a dextrorotary reducing sugar, the amount present varying from 1.65 to 4.28 per cent. Windisch (*Oesterr. landw. Vers. Wes.* 8, 74) has continued his study of the ash of paprika, and has compared the results of a microscopic analysis with the chemical results on the content of ash and sand in the samples. His former conclusions are confirmed. A high content of sand is regarded as sufficient ground for condemnation. Süss (*Pharm. C. H.* 46, 159) calls attention to the custom in the retail trade of selling underground pimento superficially colored with ochre, or

similar bodies. The adulteration can frequently be detected by a lens as well as by the examination of the ash. For the determination of artificial coloring-matter in prepared mustard and powdered mustard, the same writer (*Pharm. C. H.* **46**, 291) shakes 50 grams of the sample with 75 cc. of 70 per cent. alcohol, filters, and makes the ordinary dyeing tests. In case the wool does not take on a marked color which is altered by either ammonia or hydrochloric acid, he concludes that no artificial coloring-matter has been employed. Filter-paper is also dipped into the solution, dried, and tested with hydrochloric acid and ammonia.

*Coffee and Cocoa Preparations.*—The soluble glaze on 32 samples of roasted coffee was examined by Orth (*Z. Unters. Nahr.-Genuss.* **9**, 137 (1905)) according to the method suggested by Hilger. He finds that candied coffee produced by roasting with the addition of sugar, and so distinguished from ordinary glazed coffee, contains from 5 to 7.7 per cent. of soluble material. The standard of 4 per cent. that has been suggested as a maximum will thus not apply to candied coffee. Ottolenghi (*Atti della r. accademia dei fisiocritici* [4], **15**, (1903) 11 pp. Reprint) calls attention to the frequent use of the seeds of *Astragalus boeticus*, and suggests the microscopic detection of the latter in the portion of the sample that sinks to the bottom of water. Balland (*J. pharm. chim.* [6] **20**, 543-549 (1904)) and Puckner (*Pharm. rev.* **23**, 305-309 (1905)) discuss the determination of caffeine. A study of the chemical and microscopical nature of coffee substitutes prepared from unmalted and malted grain has been published by Prillach (*Z. Unters. Nahr.-Genuss.* **10**, 118 (1905)). Filsinger (*Z. offentl. Chem.* **11**, 8-10 (1905)) discusses the composition of "soluble" cocoa, and directs that the soluble alkalinity must be determined and not the total alkalinity, which gives too high results. The same subject is discussed by Fröhner and Lührig (*Z. Unters. Nahr.-Genuss.* **9**, 257 (1905)) and by Lührig (*Z. Unters. Nahr.-Genuss.* **9**, 267 (1905)). According to Kuhl (*Pharm. Ztg.* 631 (1905)) the microscopic examination is valueless for determining the variety of cocoa beans employed, or the presence of an excessive amount of cocoa shells. Quantitative examination alone can determine the latter point.

*Vegetables.*—Frerichs and Rodenberg (*Arch. Pharm.* **243**, 675-683 (1905)) give the results of the examination of peas at various stages of their maturity, and of canned peas, and discuss the application of the results to the inspection of the product. Riess (*Arbb. kais. Ges. A.* **22**, 663-666 (1905)) has investigated the compound formed by the action of copper salts in the greening of peas, and methods for the detection of copper. He suggests that copper may be determined by macerating with water, strongly acidifying with hydrochloric acid, and separating by means of iron. The result of the examination of frozen potatoes has been given by Parow (*Z. Spiritusind.* **28**, 405 (1905)). Wintgen (*Z. Unters.*

*Nahr.-Genuss.* **10**, 757-761 (1905)) has reported an interesting case of the swelling of canned goods without any appearance of decomposition. The examination of samples shows the excessive gas to consist largely of hydrogen, and masses of a dark colored product which proved to be chiefly phosphate of iron were found in patches at the side of the receptacle. The author concluded that the nature of the sample was due to the action of the acid upon the imperfectly plated iron, an iron salt being formed with the elimination of hydrogen.

*Fruit Products.*—The year has been marked by a largely increased number of analyses of fruit products of various descriptions for the purpose of securing data for the establishment of standards. A. Beythien (*Z. Unters. Nahr.-Genuss.* **10**, 339 (1905)) has studied the relation between the composition of fruit juices and the alkalinity of their ash. He confirms the earlier belief that the ratio of ash to alkalinity lies between 1 to 10 and 1 to 15, rather than in the neighborhood of 1 to 5.3 as has been said by Evers. A method for the preparation of fruit juices and standards of composition have been adopted by the association of German food manufacturers and dealers (*Pharm. Ztg.* 380 (1905)). A. and M. Dominikiewicz (*Z. Unters. Nahr.-Genuss.* **10**, 735-744 (1905)) called attention to the relation between viscosity and refractive index of fruit juices and fruit sirups. They believe that the determination of viscosity and index of refraction are sufficient for the examination of these products with reference to their purity. Otto and Tolmacz (*Z. Unters. Nahr.-Genuss.* **9**, 267 (1905)) find the unfermented beverages on the market to be grossly adulterated. Some are prepared from dried fruit and others are entirely artificial. Further studies regarding the normal composition of fruit juices and standards for the same have been conducted, especial attention having been given to raspberry juice. Complete analyses have been made of the products of 1905 of the various localities prepared in a different manner. The results published are of great value for the establishments of standards for the inspection of fruit products. Among the chief contributors are P. Bittenberg (*Z. Unters. Nahr.-Genuss.* **9**, 141-145 (1905)); F. Morschöck (*Z. Unters. Nahr.-Genuss.* **10**, 733-735 (1905)); E. Baier (*Z. Unters. Nahr.-Genuss.* **10**, 731-732 (1905)); A. Juckenack (*Z. Unters. Nahr.-Genuss.* **10**, 729-730 (1905)); A. Beythien and L. Waters (*Z. Unters.-Nahr.-Genuss.* **10**, 726-729 (1905)); H. Lührig (*Z. Unters. Nahr.-Genuss.* **10**, 714-726 (1905)).

*Wine.*—Windisch and Roettgen (*Z. Unters. Nahr.-Genuss.* **9**, 70-81 (1905)) have published a systematic review of the methods for the determination of volatile acids. They call attention to the fact that the arbitrary method commonly employed for this determination gives incomplete results because of insufficient distillation. They recommend that the distillate be increased

to 300 cc. They also call attention to the fact that lactic acid passes over with steam with some difficulty, and discuss its influence on the determination of volatile acids in wine. The same authors (*Z. Unters. Nahr.-Genuss.* **9**, 129-133 (1905)) studied the changes in composition of wine occasioned by the use of different clarifying agents. They conclude that the composition of wine is only slightly modified, especially in the case of isinglass and gelatin. Beneschoosky (*Z. landw. Versuchsw. Osterr.* **8**, 78-82 (1905)) called attention to the high volatile acid content of Italian wines. Out of 30 samples examined from various districts in Italy, 12 contained less than 0.1 per cent. of volatile acids, and 18 between 0.1 and 0.3 per cent. Of 913 samples of German wines examined 90 per cent. varied within the limits of 0.01 and 0.069 per cent. The amount of succinic acid in 15 samples of Italian wines is reported by Prandi (*Staz. sper. agr. ital.* **38**, 503) as from 0.0820 to 1.1103 per cent. In the majority of cases it varied from 0.03 to 0.13 per cent. Krug (*Z. Unters. Nahr.-Genuss.* **10**, 417 (1905)) determined the sodium content in a series of samples of wine. The maximum content found was 6 mg. In over 80 per cent. of the samples examined less than 1 per cent. of sodium was found. According to Partheil (*Fifth Internat. Kong. angew. Chem. Ber.* **3**, 1019-1022 (1903)) the usual method for the determination of lactic acid in wine neglects the fact that acid is volatile with steam. He suggests the precipitation of tartaric, citric, and succinic acids with barium salts. Lactic and acetic acids may be distilled from the filtrate with steam. Pairault (*Bol. Cámara Com. Asunción, Paraguay* [15] (1904)) has studied the manufacture of orange wine. As ordinarily conducted the fermentation is slow because of the absence of sufficient materials for the nutrition of the yeast cells. The writer suggests the addition of sugar and mineral salts. Kramszky (*Z. Unters. Nahr.-Genuss.* **10**, 671 (1905)) has reported the composition of raisins and discussed the same with reference to the manufacture of raisin wine. Ruff and Jeroch (*Chem. Ztg. rep.* **74**, 1905) calls attention to incomplete results obtained in the direct titration of sulphurous acid, owing to the oxidation of sulphites by the oxygen of the air.

*Distilled Liquors.*—Schidrowitz (*J. Chem. Ind.* **24**, 176-178 (1905)) discusses standards proposed for the composition of distilled liquor. He suggests as suitable maximum standards 40 mg. of total acids (calculated as sulphuric acid), 0.3 gram of fusel oil, and 0.25 gram for extract. A board of control and rigid inspection are suggested. The manufacture of alcohol from grape pomace is suggested by Perkins and Jamieson (*J. Dept. Agr. So. Aust.* **9**, 24-38 (1905)). It is stated that the pomace should give about 32 gallons of proof spirit per ton, 80 per cent. of which may be recovered by leaching and fermenting. The methods of manufacturing brandy from various fruits are



discussed by Windisch (*Deutsche Essigindustrie* 9, 89-91 (1905)) and Kayser and Dienert (*Ann. science agron.* [2] 10, 209-219 (1905)). A study of the bacterial action that occurs during the fermentation is included. Contributions to the literature of the examination of distilled liquors have been made by Hehner (*Analyst*, 30, 36-56 (1905)), Rocques (*Ann. chim. anal.* 10, 103-108 (1905)), Beckmann (*Z. Unters. Nahr.-Genuss.* 10, 143-152 (1905)) and others.

*Vinegar.*—Jonscher (*Z. öffentl. Chem.* 11, 467-473 (1905)) discusses standards for wine vinegar. He believes that little can be accomplished by analytical data. Froehner (*Z. Unters. Nahr.-Genuss.* 9, 361-363 (1905)) considers lactic acid as a normal constituent of wine vinegar, and suggests that the amount of that substance present may be of value in judging the quality of the product. For the same purpose Fresenius (*Z. Unters. Nahr.-Genuss.* 10, 121-129 (1905)) and Moslinger (*Z. Unters. Nahr.-Genuss.* 10, 125 (1905)) suggest the determination of glycerol. The amount of glycerol in wine is not reduced in the manufacture of vinegar. Maustbaum (*Revista chim. pura app.* 1905, p. 8) suggests the detection in wine vinegar of acetic acid made by the distillation of wood by means of the furfural reaction and the reduction of permanganate. The latter is believed to be the better of the two methods.

*Preservatives.*—An unusual amount of attention was given during the year to the question of detecting preservatives in food. The tendency to the quantitative detection is very noticeable. Considerable attention has been paid to the effect of preservatives on nutrition and health, and on the whole the tendency of hygienists is evidently more adverse to the use of preservatives than formerly. During the last year the subject of the determination of boric acid has proved an interesting field of work to a large number of men. The literature of the quantitative determination of boric acid has been thoroughly reviewed by Windisch (*Z. Unters. Nahr.-Genuss.* 9, 641-660 (1905)) who suggests the elimination of the difficulty occasioned by the use of two indicators with the consequent error, owing to the presence of traces of phosphoric acid that cannot be removed. He proposes the neutralization of the solution by means of iodine and thio-sulphate solution, according to Jones, and the titration of the boric acid (which is then free) with phenolphthalein as indicator. (The results of the method outlined by him, however, have not met with general satisfaction at the hands of other workers.—*Reviewer.*) Fritzsche (*Apoth. Ztg.* 20, 856 (1905)) believes that a positive reaction for boric acid by the turmeric paper test is sufficient for the condemnation of the sample, and that negative results may readily be obtained in the absence of boric acid by the use of pure reagents. Fendler (*Apoth. Ztg.* 20, 868 (1905)) called attention to the fact that boric acid may be detected in a solution con-

taining 0.005 per cent., and suggests that it should only be reported as present when a strong reaction is obtained. He believes that traces may occur in normal meat, or result from the salt employed in packing it (see this Journal, 28). He suggests (*Apoth. Ztg.* 20, 757 (1905)) that the best results are given by a solution containing 10 per cent. of hydrochloric acid, and suggests a 10 per cent. solution of ammonia for the confirmatory test. He proposes the preparation of turmeric paper by immersing strips of turmeric paper in a solution of 0.05 gram of curcumin in 100 cc. of absolute alcohol, and drying in the dark. He calls attention to the fact that the flame test is not nearly so delicate as the turmeric paper test. He suggests that where an evident flame test is obtained it is sufficient without confirmation, but states that this test is not without objection because of its subjective nature. He also suggests that in place of turmeric, safflower and marigold may be used as boric acid reagents. Goske (*Z. Unters. Nahr.-Genuss.* 10, 242-243 (1905)) suggests the method for the detection of boric acid which was originally proposed by Howard (*Science* 19, 583 (1904)) for the detection of curcumin. He states that by this method boric acid may be detected in solutions varying from 0.001 to 0.0001 per cent. (This method has also been employed by Bigelow and Brinton for the quantitative determination of boric acid.) Mezger (*Z. Unters. Nahr.-Genuss.* 10, 243-245 (1905)) proposes a modification of the flame test for boric acid. He adds to the ash in a flask 2 cc. of strong hydrochloric acid, and from 15 to 20 cc. of methyl alcohol. The flask is then attached to a reflux condenser and heated on a water-bath at least 70° for one-quarter of an hour. If hydrogen be passed through the mixture after cooling, the boric acid compound is carried with it, and may be detected by the color of the flame. O. von Spindler (*Z. Unters. Nahr.-Genuss.* 10, 478-482 (1905)) reviews the literature on the determination of boric acid and proposes a new apparatus for the flame test. Blarez (*Chem. News* 1905, p. 39) has proposed a modification of the method ordinarily employed for the detection of fluorides in wine. He finds they may be more completely precipitated by barium salts than by calcium salts, and suggests the addition of barium acetate after adding a small amount of soluble sulphates. The precipitate is settled by centrifuging, separated by filtration, and ashed, after which the usual method is employed. The influence of formaldehyde on fermentation has been studied by Hirsch (*Allgem. Z. Bierbrauerei Malzfabrik.* 1905, Aug.) and new methods for the detection of formaldehyde, or modifications of old methods have been proposed by Lyons (*Pharm. J.* 75, 443 (1905)), Voisenet (*Bull. soc. chim.* 33, 1198-1214 (1905)) and Nicolas (*Compt. rend.* 58, 697-698 (1905)). The last-named suggests that the greenish fluorescence obtained in milk containing formaldehyde by the addition of amidol will permit the

recognition of the preservative in quantities of 1 to 500,000, or less. Before applying the reagent the milk is clarified with acid, and the filtrate is employed. Schuch (*Z. landw. Versuchsw. Oesterr.* 8, 1058-1060 (1905)) made a comparative study of methods for the detection of formaldehyde and gave his preference to that of Arnold and Mentzel. Considerable attention has been given during the year to the use of hydrogen peroxide as a preservative. The literature of the subject has been reviewed by Lukin (*Centr. Bakt.* 15, 20-32 and 165-174 (1905)). E. von Mahler (*Chem. Ztg.* 29, 32 (1905)) proposes the detection of saccharin by fusing the residue from the ether extract with sodium or potassium, extracting the sulphide so prepared from the charred mass by means of water and pouring the solution into a solution of sodium nitroprusside. The red-violet color so obtained is a certain indication of the presence of saccharin since no other compound containing sulphur and soluble in ether is present in food. Grimaldi (*Staz. sperim. agron. ital.* 38, 618 (1905)) gives the results of the quantitative determination of salicylic acid in several fruits, and a partial review of the literature relating to the distribution of salicylic acid in nature. The disappearance of sulphurous acid in wine is discussed by Carles (*Rep. Pharm.* [3] 17, 97-102 (1905)). Methods for the determination of sulphurous acid in foods were compared by Schumacher and Feder (*Z. Unters. Nahr.-Genuss.* 10, 649-659 (1905)). The ordinary method of distillation was found to give satisfactory results. The suggestion that the results obtained by the method are influenced by the sulphur content of illuminating gas used in the operation was put to a severe test. It was found that no inaccuracy was occasioned by the gas burned in the room in which the operation was conducted.

*Meat Products.*—The methods for the determination of salt-peter in meat preparations have been studied by E. Crespolani (*Bull. chim. farm.* 44, 697-700 (1905)), K. Farnsteiner (*Z. Unters. Nahr.-Genuss.* 10, 329 (1905)), and W. Stüber (*Z. Unters. Nahr.-Genuss.* 10, 330 (1905)). It has been shown that when 1 gram of potassium nitrate is added to 300 grams of meat it is reduced first to nitrite and then to ammonia. The Ulsch method was found to be entirely unreliable for the determination of potassium nitrate because of the effect of the reagents on proteids. By the Schlösing-Wagner method from 99.58 to 102 per cent. of the nitrate present was recovered. E. Carlinfanti and A. Manetti (*Archivio di farmacol. sperim. scienze affini*, 4, heft 7-8) made a systematic examination of canned meats for the Italian army. They regard canned meat as less digestible than fresh meat and explain the repugnance that has been experienced after a continuous diet of canned meat to its large fat content. Ground cereal products have been reported by H. Matthes (*Z. Unters. Nahr.-Genuss.* 9, 732 (1905)) as adulterants for corned beef. M. Toyonaga (*Bull. Col.*

*Agr. Tokyo Imp. Univ.* **6**, 89-95 (1904)) has summarized the results of other investigators with reference to the calcium content in the different animal tissues, and discussed its relation to magnesium. Klikton (*Z. Unters. Nahr.- Genuss.* **10**, 159 (1905)) has investigated the number of errors in the determination of sulphites in meat, owing to the sulphur content of the gas employed. He finds that in a room of 109 cubic meters no appreciable amount of sulphurous acid could be detected after nine gas burners had been employed for ten hours.

*Meat Extract.*—M. Siegfried and E. Singewald (*Z. Unters. Nahr.- Genuss.* **10**, 521-527 (1905)) pointed out that the deterioration of meat extract is accompanied by the conversion of organic phosphorus into the inorganic form. After a series of analyses of extracts of known origin they suggest that the quality and age of an extract may be judged by estimating the total phosphorus and organic phosphorus. K. Micko (*Z. Unters. Nahr.- Genuss.* **10**, 393 (1905)) has applied Fischer's ester method of hydrolyzation to the determination of the presence of polypeptids in meat extracts. Kutscher (*Centr. physiol.* **19**, 504 (1905)) has made a careful study of the various meat bases in meat extract. He concludes that such products do not have a uniform composition and bodies are sometimes found in it which are not necessarily constituents of muscular tissue. He identified ignotine, methylguanidine, carnomuscarine, neosine, novaine, and oblitine. Barral (*J. pharm. chim.* [6] **22**, 392-395 (1905)) reports the analysis of a so-called papayin meat powder.

*Separation of Proteids.*—H. C. Haslam (*J. Physiol.* **32**, 267-298 (1905)) has suggested new methods for the separation of proteid bodies which he regards as more exact than those commonly employed. He believes that the methods now in use afford results that are far from satisfactory, owing to the tenacity with which the various proteid bodies cling to each other. This tenacity he explains by the supposition that a loose chemical composition exists among them resulting in chemical equilibrium, which is upset by the addition of a precipitant with the result that only a partial separation is effected, some of the soluble proteids going into the precipitate, and some of the insoluble proteids remaining in the filtrate. Important contributions to the literature on the hydrolysis of proteids and the cleavage compounds formed have been made by Z. H. Skraup (*Monatsh. Chem.* **26**, 243-264 (1905)), A. Kossel and Dakin (*München. Med. Wochenschr.* **51**, 545 (1904)), F. Dubrowin (*Inaug. Diss.* St. Petersburg, 1902), and Hayashi (*Arch. Expt. Path. Pharmacol.* **52**, 289 (1905)). R. Steinegger (*Landw. Jahrb. Schweiz*, **19**, 512-527 and 528-529 (1905)) has studied the influence of formaldehyde on casein and other proteid bodies. The increased acidity caused by the addition of formaldehyde to milk is explained by the formation of a compound which is free from the amphoteric

character of the proteid body. The carboxyl groups present, therefore, have their full value and may be titrated. The growing practice of polishing barley and peas has received considerable attention. Forster (*Z. öffentl. Chem.* **11**, 36 (1905)) shakes the suspected sample with chloroform and examines the sediment microscopically. If talc is found to be present, 5 grams of the sample are ignited and the ash fused with soda and saltpeter. The magnesium is determined in the fused residue and calculated to talc ( $H_2Mg_3Si_4O_{12}$ ). In this way the small amount of magnesium naturally present is also considered to be derived from talc. This slight inaccuracy is avoided by Matthes and Müller (*Z. öffentl. Chem.* **11**, 76 (1905)) who shake 50 grams of the barley with water (using from 500 to 600 cc. in all), pour off the supernatant liquid after twenty-four hours, and dry and ignite the residue. The ash is examined microscopically, extracted with hydrochloric acid to remove magnesium that may have come from the outer surface of the barley, and the insoluble portion treated with hydrochloric acid and magnesium determined. Of 53 samples of rice examined by E. v. Rannier (*Z. Unters. Nahr.-Genuss.* **10**, 745 (1905)) 40 were coated with talc and 25 were also treated with a blue dye for the purpose of neutralizing the natural yellowish tint of the rice. Hefelmann (*Z. öffentl. Chem.* **11**, 309) confirms in a general way the results mentioned above. He suggests as provisional maximum limits for talc 0.3 per cent. and 0.2 per cent. for rice and barley, respectively. In several laboratories attention has been given to the study of methods for the determination of glucose and prepared foods. The fermentation methods have been studied by von Raumers (*Z. Unters. Nahr.-Genuss.* **9**, 705 (1905)) who compares the results obtained by fermenting with different varieties of yeasts. He found that compressed yeast is not suitable for this purpose because of the lack of uniformity among different varieties, leading to a corresponding lack of uniformity in the results of different laboratories. He considers that wine and fruit yeasts are not applicable because of their failure to ferment maltose, resulting in too high a figure. Of the yeasts he employed, the bottom fermentation—beer yeast—is the only one he regarded as satisfactory for this purpose. This yeast ferments maltose completely, but leaves dextrose unfermented. E. Ewers (*Z. öffentl. Chem.* **11**, 407 (1905)) recommends the quantitative determination of starch by means of the polariscope after first making the starch soluble by means of acetic acid, dilute hydrochloric acid and hot water. He finds the polarization of wheat, rice and maize starch to be equal, but that of potato starch to be somewhat higher.

#### FATS AND OILS BY L. M. TOLMAN.

Investigations by Winkel (*Z. Unters. Nahr.-Genuss.* **9**, 90-96 (1905)) lead to the conclusion that the changes other than ran-

idity which take place in fat exposed to the sunlight are different from those which take place in the dark, but that in both cases the changes are due to chemical action. He also concludes that rancidity in fat is due to micro-organisms. Soltzien (*Chem. Rev. Harz. Fettind.* 12, 177 (1905)) proposes to detect rancid butter by means of Welman's reagent, which he applies directly to uncolored butter, while with colored butters he first distills with steam and applies the test to the distillate. Klimont (*Chem. Rev. Harz. Fettind.* 12, 160 (1905)) has reviewed the processes taking place when a fat becomes rancid. Petersen (*Chem. Ztg. Rep.* 181, 1905) has been able to change oleic acid into stearic by means of electrolysis. By dissolving 10 grams of oleic acid in 150 cc. of alcohol and adding 3 cc. of dilute sulphuric acid (1-4) and using a nickel cathode and a platinum anode in a porcelain cylinder, and passing a current of 1.35 amperes and 20 volts for four hours, the solution being kept at 30-35°, he was able to obtain a heavy precipitate of stearic acid. A number of papers on the unsaturated fatty acids and the addition (J. Moll van Charante: *Chem. Centr.* 1, 1309 (1905)) and oxidation products (Alex. Saytzeff: *J. Pharm. Chem.* 71, 422 (1905)) have been published. Von Molinari and Souccini (*Chem. Ztg.* 715 (1905)) have studied the action of ozone on linseed oil and found that one molecule of oleic acid absorbs three molecules of ozone while one molecule of linolic acid absorbs two molecules of ozone. This absorption the authors found to be quantitative and they propose a new number to be used in the analysis of fats to be known as the ozone number. Frank and Kamenetzky (*Chem. Centr.* 1, 696 (1905)), *Chem. Ztg. Rep.* 75, 1905) have prepared some extensive tables of the physical and chemical constants of oils, fats and waxes. New methods for the determination of the physical constants of oils and fats have been proposed by Rakusin (*Chem. Ztg.* 841 (1905)) for the specific gravity and Ubbelohde (*Z. angew. Chemie* No. 24, 1905) for the melting-point, while Farnsteiner (*Z. Unters. Nahr.-Genuss.* 8, 407 (1905)) has studied the index of refraction and adopts the correction for temperature change of 0.000365 for 1° C., the same as adopted by the Association of Official Agricultural Chemists in this country. Deiter (*Arb. hyg. chem. Unter.* Heft 29 (1905)), in a study of the different methods for the determination of the iodine number of oils, reached the conclusion that the Hanus method was the most satisfactory and that ten to fifteen minutes was a sufficient time for the reaction to take place. The value of an examination of the unsaponifiable matter of fats has been shown by a number of investigations. On account of the effect of the food of the animal on the fat it is often impossible to place any confidence in the color tests, and the determination of the presence of phytosterol is the final test. Olig and Tillmanns (*Z. Unters. Nahr.-Genuss.* 9, 65 (1905)) have shown, however, that the addition of a slight trace of paraffin

to the fat under examination made the phytosterol acetate test of Bomer of practically no value as the paraffin reduced the melting-point of the acetate to about  $100^{\circ}$ , but Polenske (*Arb. Kais. Ges. Amt.* 22, 557-576) has shown that it is possible to detect this small amount of paraffin by treating the fat with strong sulphuric acid which carbonizes the fat but does not attack the paraffin. Fischer and Peyau (*Z. Unters. Nahr.-Genuss.* 9, 81 (1905)) found that sulphurous acid would destroy the substance that gives the Halphen reaction in cottonseed oil and that the only way to detect oils treated in this way is by the phytosterol acetate method of Bomer. The Halphen test has been considered a specific test for cottonseed oil but it has been shown that Kapok and Baobab oils give the reaction which in fact seems to be characteristic of the oils of the *Malvaceae* (P. Soltsien: *Chem. Centr.* 2, 1133 (1905)). A number of new methods for the detection of coloring-matter in fat have been proposed. Sprinkmeyer and Wagner (*Z. Unters. Nahr.-Genuss.* 9, 958 (1905)) extract the color from a petroleum ether solution with glacial acetic acid. Arnold (*Z. Nahr.-Genuss.* 10, 239 (1905)) uses an acid alcohol (1 cc. HCl to 99 cc. of 95 per cent. alcohol). He takes 5 cc. of the melted fat and 2 cc. of the alcohol and heats until the solutions mix. The alcohol dissolves the color and collects on the surface of the fat. Fendler (*Chem. Rev. Fett. Harzind.* 1905, 207-237) uses a mixture of nitric acid in ether as a reagent for the determination of added color. Sprinkmeyer and Wagner (*Z. Unters. Nahr.-Genuss.* 10, 347-353 (1905)) have made a study of sesame oil and give the analyses of a number of oils from different countries. Aparin (*Zhur. Russ. Fiz. Khim. Obshch.* 36, 581-596 (1904)) has studied the composition of the oil of the strawberry and finds it to be largely linolic and linolenic acids with only a trace of oleic acid.

#### DAIRY PRODUCTS BY L. M. TOLMAN.

There have been several valuable papers on the effect of the food on the composition of milk: One (Morgen C. Berger and G. Fingerling: *Landw. Vers. Stat.* 62, 251-386 (1905)) tending to show that where the ration is normal but restricted in quantity the addition of fat and protein to the ration has a favorable effect on the milk production. Fat exerts a specific influence on the production of butter fat while protein shows no such specific action. An addition of carbohydrates to the ration was without influence on either the total yield of milk or the production of butter fat. The conclusion is drawn that food fat is especially suited to the formation of milk fat and that perhaps up to a certain limit cannot be replaced by other food constituents. Other work (T. Pfeiffer, A. Eïnecke and W. Schneider: *Mitt. Landw. Inst. Breslau.* 3, 179-225 (1905)), in which such substances such as a mixture of asparagine and cane-sugar were substituted, in quan-

tities having equal fuel values, for a part of the proteids in a ration rich in proteids, showed no decrease in the quantity of milk but a lowering in the percentages of fat, protein and total solids and a decrease in the actual yield of fat, from which it is concluded that asparagine and the amides in general are not nutrients but sometimes act as stimulants to increase the yield of milk but always at the expense of the other food constituents or the body tissues. Jensen (*Landw. Jahrb. Schweiz.* **19**, 534-559 (1905); *Rev. gén. lait.* **5**, 103-110 and 121-128 (1905); **5**, 152-161, 178-185, 198-205 (1906)) calls attention to the fact that with the feeding of large quantities of saltpeter a trace of nitrate is found in the milk; that feeding large quantities of roots increased the amounts of volatile acids in the butter fat, and the feeding of sesame cake increased the content of oleic acid in the milk fat. The general conclusion of all the work is that the composition of the milk and of the milk fat is influenced to a marked degree by the food. Richmond (*Analyst*, **30**, 325-329 (1905)) gives data showing the average composition of 15,910 samples of milk. This was as follows: Specific gravity, 1.0322; total solids, 12.68 per cent.; fat, 3.75 per cent.; and solids, not fat, 8.94. As an interesting comparison with this are the results on the composition of milk of sheep by Sanna (*Staz. sper. agr. ital.* **38**, 289-306 (1905)) which shows the specific gravity to be 1.0385, total solids 18.34 per cent., fat 7.53 per cent., casein 4.65 per cent., albumin 1.01 per cent., sugar 4.05 per cent., and ash 0.89 per cent., or solids, not sugar, 10.60 per cent. The question as to the changes that take place in the composition of milk during souring is often of importance to the inspection chemist as the samples are in most cases changed before the analysis is made. In order to test this Thorpe (*Analyst* **30**, 197-205 (1905)), of the government laboratory of England, had 13 samples of fresh milk kept for periods varying from two to fourteen and one-half weeks and found that the fat content decreased on the average only 0.06 per cent. The loss of solids not fat in the same time was from 0.24 to 0.87 per cent., due mainly to the production of alcohol and volatile acids. These results show that for inspection purposes the analysis of the sour milk is satisfactory in judging the character of the fresh milk. The changes that take place in milk on sterilization and the effect of the sterilization of the milk on digestion, especially of infants, have been the subject of much study, and the results seem to show that the raw milk is more digestible although Brunon (*Bull. acad. med.* [3] **53**, 396-399 (1905)), in his report of the work of the infant milk depot at Rouen which has during the last four and one-half years fed 2,000 infants, 70 per cent. of whom suffered from malnutrition, finds that only a very few of the children failed to do well on sterilized milk. The sterilization was accomplished in an autoclave at 102° C. Jensen and Plattner (*Ann. Agr. Suisse*, **6**, 205-223 (1905) *Rev. gén. lait.* **4**, 361-368, 388-397,



419-424 (1905)), in an extensive study of the effects of heating milk for various lengths of time and at different temperatures found that marked changes took place in the chemical composition of the milk, and concluded from their work that in order to retain the properties of the raw milk the heating in sterilization should not exceed 70° C., which is sufficient to destroy pathogenic bacteria.

O. Laxa (*Milchw. Zentbl.* **1**, 538-547 (1905)), in a study of casein and paracasein, finds that lactic acid unites with casein to form lactates and that under the influence of acids paracasein changes to casein. He found that lactates that contained 1 per cent. or less of lactic acid were insoluble in water while those of higher content were soluble. He was able to prepare lactates that contained as high as 7.5 per cent. of acid. He concludes that the monolactates and dilactates of Van Slyke and Hart are untenable, a conclusion that these authors have reached in their later work. He explains the curdling of milk by the formation of lactic acid which changes the phosphates of the milk into acid salts and the precipitation of the soluble lactates by the mineral acid. Laquer (Abs. in *Osterr. Chem. Ztg.* **8**, 521 (1905)) found that paracasein contained more carbon and hydrogen than casein but 0.8 per cent. less nitrogen, that it had the same acidity as casein but was more readily precipitated by salts. Porcher (*Compt. rend.* **141**, 73-75 and 467-469 (1905)), as the result of his studies on the physiology of the mammary gland, concludes that the transformation of glucose into lactose is a function of this gland. Methods for the estimation of fat in milk have been the subject of a great deal of study during the last year. The Gottlieb-Rose or the Sichler "sin-acid" methods both seem to be very promising. A number of chemists have given the Gottlieb-Rose method a thorough trial in comparison with the standard methods and have in all cases found it to give reliable results. Thomsen (*Mealkeritid.* **18**, 356-359 (1905)) showed that it was not necessary to peptonize the milk to obtain complete extraction with the Gottlieb-Rose method while unless this is done with the ordinary method of ether extraction low results are obtained. Burr (*Z. Unters. Nahr.-Genuss.* **10**, 286-290 (1905)) considers that the method is applicable to all dairy products. The results on the "sin-acid" method of Sichler have not been so uniform, some chemists finding it as satisfactory (Lotterhos: *Molk. Ztg.* **19**, 145-146 (1905)) as the Gerber method and others not entirely satisfactory (M. Klassert: *Z. Unters. Nahr.-Genuss.* **9**, 12-15 (1905)). Unfortunately, the reagent used in this test is a secret so that the application and improvement of the method is likely to be slow. The advantage of a method, which does not use an acid to dissolve the proteids of the milk, as is the case in the Gerber and Babcock methods, in the analysis of such products as sweetened condensed milk where the acid chars the cane-sugar so that the

method is not applicable, can be readily seen. The use of a fine sponge as the absorbent material in milk analysis has been tried by Bellier (*Ann. chim. analyt.* 10, 268-276 (1905)) with success. The sponge was first extracted with dilute hydrochloric acid, alcohol, ether and water and dried. The weight of the sponge prepared in this way remains practically constant. The milk is transferred to the sponge and dried to constant weight, extracted with ether for the fat, treated with formaldehyde to render the proteids insoluble, this is washed with 50 per cent. alcohol containing 5 per cent. of acetic acid and water to remove the sugar and ash thus giving him a complete analysis of the milk on one sample. Another ingenious method has (F. Bordas and Touplain: *Ann. chim. analyt.* 10, 267-268 (1905); *Rev. soc. sci. hyg. aliment.* 2, 163-168 (1905)) been proposed for making an analysis of milk on a single portion; 10 cc. of milk are added drop by drop to a centrifuge tube containing 25 cc. of 65 per cent. alcohol acidified with acetic acid and after standing for a few minutes the tube is whirled. The supernatant liquid is poured off and the sugar determined in it. The residue in the tube is extracted with ether several times, whirling each time to settle the insoluble material and decanting the ether, which is evaporated and weighed. The residue in the tube is dried and weighed as casein. The detection of added water in milk is one of the most important determinations that the chemist has to make in the inspection of milk supplies, and the specific gravity and index of refraction of the milk serum have been found of great value in detecting this form of adulteration. Bialon (*Milchw. Zentbl.* 1, 499-502 (1905)) has shown that the method employed in preparing the serum makes considerable difference in its specific gravity. In one case the serum obtained by spontaneous coagulation had a specific gravity of 1.0284, that where acetic acid was used 1.0266, and that prepared by rennet 1.0291. This he explains by the different amounts of phosphates, lime, and proteids left in solution. The serums prepared by the same method did not give uniform results and better results were obtained by the following formula:

$$\sigma = \frac{100s - f}{100 - \frac{f}{0.933}}$$

in which  $s$  represents the specific gravity of the milk,  $f$  the percentage of fat, and 0.933 the average specific gravity of milk fat. For pure milk  $\sigma$  or the specific gravity of the fat-free milk was found to be about 1.0323. On the basis of a large number of determinations, the author concludes that a specific gravity of 1.0323 or above calculated by this formula shows that the milk is unadulterated, while a lower figure shows that water has been added. The method is, of course, not applicable to curdled milk.

This difference in the serum would affect the results by the index

of refraction in the same way. The best method of preparing the serum, according to Henseval and Mullie (*Rev. gén. lait.* 4, 529-538 (1905)), is to add 1 cc. of 20 per cent. acetic acid to 50<sup>+</sup> cc. of the milk, heat on a water-bath to 65-70° for five minutes, cool to 15°, filter, read the index of refraction at room temperature and calculate to 15° by the factor 0.000117 for each degree centigrade. The same result has been attempted by the determination of the freezing-point of the milk and a number of chemists have obtained very uniform figures for this test. Allermann (*Landw. Jahr.* 19, 499-502 (1905)) found that the average freezing-point of 23 samples of milk was -0.571° C., Barthel (*Rev. gén. lait.* 4, 505-512 (1905)) found it to be very constant between -0.55° and -0.57° C. Bomstein (*Russ. Vrach.* 3, 3 (1905)) claims to be able to detect 5 per cent. of added water and Lajoux (*Ann. chim. anal.* 10, 210-231 (1905)), from his work, suggests a standard for market milk of -0.55° to 0.57°. It must be remembered, however, that such substances as glycerol (*Ann. chim. anal.* 10, 89-90 (1905)), sodium bicarbonate and formalin influence these results very much. The presence of nitrates in the milk as a test for added water is not always (J. Adorjan: *Z. landw. Vers. Oesterr.* 8, 846-851 (1905)) to be relied on as a little dirt in the milk or the water used in washing the cans may cause the milk to give the reaction. The presence of ammonia in milk (Trillat and Sauton: *Ann. inst. Pasteur.* 19, 494-502 (1905)) is also an indication of added water and may be detected by the nitrogen iodide test as follows: Ten cc. of the milk are placed in a test-tube and treated with 10 cc. of a 10 per cent. solution of iodine trichloride. The filtrate is carefully neutralized with lime water; when in the presence of ammonia a black precipitate of nitrogen iodide soluble in an excess of the reagent is formed. The value of a preservative which does not change the amount of solids or ash in the milk for preventing changes in milk kept for analysis is evident and some results by Hoft (*Chem. Ztg.* 29, 54 (1905)) show that formalin to the extent of 4 drops to 100 cc. does not affect the percentage of solids, but larger amounts cause an appreciable increase. Seligmann (*Z. Hyg. Infektionskrankh.* 49, 325-328 (1905)) proposes the use of Schiff's reagent for the detection of formalin in milk. He adds 2 to 3 drops of sulphuric acid to 5 cc. of the milk and then adds the reagent which gives a violet-red color in the presence of as little as 1:40,000. Utz (*Milchw. Zentbl.* 1, 175-178 (1905)) detects the presence of hydrogen peroxide in milk by the use of titanous and vanadic acids.

The collection of data as to the variability of the composition of butter fat shows two reports on Holland butter: one, that of Van Sillevoldt (Abs. in *Z. Unters. Nahr.-Genuss.* 9, 734 (1905)) gives out of 3945 samples examined during January, February and March, only 4 samples that had a Reichert-Meissl number under 24, while in the three months preceding, 32 samples fell

below, while Bemelman's report (*Contribution à l'étude de la variabilité des constantes des beurres néerlandais*. Bréda, 1905, pp. 81; Abs. in *Rev. gén. lait*. 4 No. 22, pp. 521-522 (1905)), on the butter of 485 Holland cows shows that the Reichert-Meissl number quite generally fell below 24.

The question whether feeding sesame cake to cows will cause the butter to give the Baudoin reaction is of great importance in countries which require that sesame oil shall be added to oleo-margarine. Denoel (*Bull. Agr.* (Brussels) 21, 183-192 (1905)), in some recent experiments, was unable to find a trace of a test in the butter from cows fed on sesame cake. This is contrary to the results of many other experiments, and to what might be expected from the results that have been obtained by feeding cottonseed meal. The detection of cocoanut oil in butter has received a good deal of attention. Jensen (*Landw. Jahrb. Schweiz*, 19, 477-495 (1905); *Ann. Agr. Suisse*, 6, 224-246 (1905); *Rev. gén. lait*. 4, 437-447, 457-464, 481-490 (1905)) has studied the volatile acids of cocoanut oil and of butter fat and finds that cocoanut oil contains no butyric and very little caproic acid, while butter on the average contains 3.92 per cent. butyric and 1.88 per cent. of caproic acid. Kirshner (*Z. Unters. Nahr.-Genuss*. 9, 65-70 (1905)) applies this work of Jensen and separates the caprylic acid which is the chief acid of cocoanut oil from the butyric acid by the use of its silver salts.

An interesting paper by Eckles and Rahn (*Centr. Bakt.* 14, 676-680 (1905)), on the changes taking place in Hartz cheese, shows that of the total nitrogen in the ripe cheese 86.2 per cent. is in the form of albumoses and peptones, 6.7 per cent. exists as amides, 3.5 per cent. as ammonia, and 3.6 per cent. as insoluble proteids, showing a much higher percentage of water-soluble proteids than occurs in Camembert and other kinds of cheese. The changes taking place in Edam cheese in the process of ripening have been studied (F. W. J. Boekhout and J. J. O. de Vries: *Centr. Bakt.* 2 Abt., 15, 321-334 (1905)) and the amount of insoluble lime is considered of great importance.

### NEW BOOKS.

GENERAL INORGANIC CHEMISTRY. By ALEXANDER SMITH. New York: The Century Co. 1906. xviii+780 pp. Price, \$2.25.

It is a difficult, if not impossible, task to give, within the bounds of a review, an even approximately adequate idea and criticism of this comprehensive and important text on general chemistry.

Professor Smith has succeeded in including in his book, of comparatively small external dimensions, all that is given in the largest college texts on descriptive, inorganic chemistry, and a

fairly complete course on elementary physical chemistry as well. This has been accomplished by a rare combination of conciseness of expression with such good judgment that nothing essential for clearness is omitted. It is not too much to say that every one of the 766 pages of text shows unmistakable evidence of careful deliberation and of original thought. No one could fail to recognize that it must have taken years to compile this book and to weld it into one homogeneous whole, even though the author had not stated in his preface that "the first draft was written six years ago" and that it is the outgrowth of a course in chemistry which he has given for fifteen years.

It is natural, in fact inevitable, to compare this book with the translation of Ostwald's "Grundlinien." In spite of the difference in size, the two contain practically the same number of pages, the same amount of information on a page, and about the same subjects. It is evident that Smith agrees in the main with Ostwald in what should be taught, and in how to teach it, but there is no trace of plagiarism or even of imitation. Such close correspondences as occur result from the fact that there is but one best way to present certain subjects, and Smith has ample grounds to trust to the merits of his own work and not adopt some other way merely to create a deceptive atmosphere of novelty.

The book is full of suggestions and of pithy phrases, valuable to teachers as well as students. For instance, objection is offered to the common expression a "gas disobeys the law." Smith says: "Our procedure, in such cases, is always more logical than our language, for we never attempt to cure a gas of its error, but always the law itself by suitable modification in its phraseology." Again: "There is no such thing as a final explanation. An explanation in science never professes for a moment to give the reasons for any occurrence. We simply don't know why behavior in nature is as it is," and he defines explanation as, "a description in greater detail." He relegates the familiar statement "the mass of the universe is a constant" to metaphysics, as something transcending experience. He makes some statements, notably in his definitions, "an element is . . . a kind of matter which never exists alone," and "a simple substance . . . contains but one element combined with a certain quantity of energy," which smack enough of metaphysics to be questionable, judging them according to his own standard. The objection to the term

chemical equation, and the substitution of a single arrow for the equality mark is an innovation which the reviewer frankly doesn't like. On page 55 we read, "...the chemical equation is not an algebraic expression; it is subject to none of the rules of algebra." But on page 78 two equations are added, and terms common to both sides are canceled, as is the universal custom in handling energy equations.

It is worthy of particular notice that the chapter on the atomic hypothesis begins on page 217. One must study the book to realize how much chemistry the student is required to learn before he is trusted with this useful but dangerous implement of thought. In this portion of the book the author is at his best, developing a caustic humor, a terseness and an effective sarcasm, which makes more interesting reading than a novel. It is impossible to refrain from an illustrative quotation. "The egregious misconception that sulphuric acid is shown by this action to be 'stronger' than hydrochloric acid was disposed of, so far as the science was concerned, half a century ago. But it survives in suburban chemical circles with remarkable tenacity." It would be a fascinating occupation to discuss the book in detail, quoting many of the characteristic and clever expressions, but space forbids.

The first 530 pages are devoted to the non-metallic elements and the general principles, and the last 236 pages to the metals. The description of potassium is begun on page 548. This does not mean that the metals are neglected by any means. They are as thoroughly treated as one could wish. There is more on steel than in any other book for beginners. But the distribution of the available space and time is what is significant, illustrating the change which has been necessitated in the teaching of beginning chemistry in recent years owing to the introduction of so many fundamental, valuable, indeed indispensable principles and theories which comprise what is well named general chemistry, what might perhaps even better be called universal chemistry (translating literally the German 'Allgemeine Chemie'), because they find application in every branch of the science to-day. Many, educated under the old régime, are unable to understand why the progress of the first course is so slow when measured in terms of the number of substances taken up. A careful perusal of this book would go far to explain the phenomenon to them.

Misprints are remarkably few in number and insignificant in kind. The absence of these faults, so common in a first edition, is but another indication of what is apparent throughout, that no labor has been spared. It is therefore surprising that the index is deplorably poor. When one finds "sulphocyanates, see thiocyanates" and then finds "thio-, see sulpho-" he is apt to become discouraged. Moreover, it ought to contain at least twice as many titles as it does, to facilitate reference to the great quantities of information. It is to be hoped that the second edition, which will probably not be long in coming, will contain an index worthy of the rest of the book.

It is a serious question whether Smith has not carried a good thing a little too far, whether he has not, after all, developed his general physical chemical principles beyond what is advisable for beginners. For example, the mathematical expression of Ostwald's dilution law and the integrated expressions for reactions of the first and second order, to determine the reaction constants, really belong in a more advanced course. In the opinion of the reviewer the book contains somewhat more than the maximum amount of information which can be introduced into the minds of the average university Freshman in a course consisting of three lectures and two two-hour laboratory periods a week extending through one college year. But the use of large type for the most important portions, and of small type for the less important, the prominent headings, the summaries of principles and the lists of questions and problems at the ends of chapters, will make it easy to select topics and utilize the book in shorter courses.

For some, the adoption of this book will necessitate a thorough-going revision of lectures, and a good deal of hard work. But it is to be hoped, for the sake of the subject of chemistry, that this may not delay its coming into general use. The reviewer gladly acknowledges that he has derived much profit from the careful study which he has given the book. It is a most admirable text and one destined to become a standard.

S. LAWRENCE BIGELOW.

**AN ELEMENTARY LABORATORY COURSE IN CHEMISTRY.** By FRANK B. KENRICK, Lecturer in Chemistry, and RALPH E. DE LURY, Fellow in Chemistry, University of Toronto. Toronto: Morang & Co. 1905. vi+90 pp. Price, \$1.00.

"The course of Practical Chemistry outlined in this book is

intended for students who are beginning the subject and . . . [are] taking a course of lectures on general chemistry." The titles of the main sections are as follows: Solution and Crystallization; Separation by Solution; Experiments with Air; Combustion of Magnesium; Properties of Magnesium Oxide; Chemical Substances; Composition of Water; Weight of Hydrogen Evolved when Magnesium Dissolves in an Acid; Law of Reacting Weights; Properties and Composition of Acids; Acids, Bases and Salts; Solubility; Separation by Volatilization; Properties of Aqueous Salt Solutions; Quantitative Separation by Solution; Precipitation of Copper; Proportion of Copper in Copper Oxide; Chemical Reaction in Solution; Measurement of Liquids; Volumetric Analysis; Law of Reacting Weights in Solution; Volume Relations of Gases; Some Experiments to Illustrate the Influence of Conditions on Reactions; A Reversible Reaction; The Mass Law; Applications of the Mass Law; Dissociation of Salts in Water; Some Experiments on Dissociation; Application of Mass Law to Dissociation; Separation and Identification of Substances; Solubility Tables; Principles of Qualitative Analysis; Separation of "Group I;" Separation of "Group II B;" Analysis of a Silver Coin.

Part II deals with elementary qualitative analysis, and in an appendix some additional explanatory paragraphs, containing also a few experiments, are given.

The old style of laboratory manual dealt almost exclusively with descriptive chemistry, and the work based upon it contributed nothing to the student's knowledge of the laws and principles of chemistry and therefore little to his mastery of the subject as a science. The great majority of existing manuals are still of this one-sided kind. A few make a more or less definite attempt to teach the science as it is. The present work is noteworthy in that, as may be seen from the titles of the chapters, it is arranged entirely with a view to emphasizing the principles of experimental chemistry. Much of the subject-matter of descriptive chemistry will be found in it—more than forms the whole content of many other manuals—but it is all arranged primarily to illustrate the principles. The directions, remarks, and questions, which, with the practical work and the head work of the pupil that they demand, constitute a clear study of each topic, are all elaborated with an admirable ingenuity which leaves nothing to be desired. Teachers of general inorganic



chemistry will find the book a most instructive and suggestive one.

In matters of detail some criticisms will occur to the reader. For example, the quantitative experiments on the composition of water and on the weight of hydrogen displaced by a given weight of magnesium give, in the hands of beginners, results so inaccurate that their usefulness is thereby largely destroyed. Again it is unfortunate that arbitrary words like *hydrogenion*, *cupricion*, and *leadion* should be employed when a logical system like Walker's is already in use by chemists. But these details do not materially obscure the very pronounced merits of the book.

A. S.

THE CHEMISTRY OF PAINTS AND PAINT VEHICLES. By CLARE H. HALL, B.S. New York: D. Van Nostrand Co. 1906. 134 pp. Price, \$2.00.

This is a book written by a chemist engaged in the manufacture of paints and colors, and gives what, in the judgment of the author, are the best methods for determining the various substances which practically occur in ordinary paints. As a rule only one method is given for each substance, and a good working knowledge of analytical methods is assumed. The book would be better if more details were given, or if there were references to standard works; but on the whole it may be said that the book is useful, indeed valuable, to any one engaged in such work. Probably any other chemist will believe some method not given here better than the one given; but by being rigidly confined to one method for each substance, the book is made compact and intelligible. In the judgment of the reviewer, some valuable methods are omitted, *e. g.*, McIlhiney's method for separating turpentine, etc., and the use of the polariscope and refractometer in detecting adulterations in liquids; also Langmuir's method for shellac. On the whole, the book is a good book and would be better if there were more of it. The most common failing of the specialist is that of forgetting that what is well-known to him is not familiar to his readers; because no book is written for specialists only.

A. H. SABIN.

### RECENT PUBLICATIONS.

ELECTROCHEMISTRY OF ORGANIC COMPOUNDS. By Walther Löb. Trans. from the author's enlarged and revised third edition by H. W. F. Lorenz. New York: J. Wiley & Sons. 1906. 10+308 pp. \$3.00.

INTRODUCTION TO GENERAL INORGANIC CHEMISTRY. By Alexander Smith. New York: Century Co. 1906. 18+780 pp. \$2.25.

ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By Harry C. Jones. New York: D. Van Nostrand Co. 1906. 9+212 pp. \$2.00.

GLUES AND CEMENTS. HANDBOOK ON ADHESIVES AND FILLINGS FOR WORKSHOP USE. By H. J. S. Cassal. London: L. U. Gill. 1906. 102 pp. 1/.

FOOD PRESERVATIVES. By R. G. Eccles. London: K. Paul. 1906. 5/.

ARCHITECTURAL HARDWOOD FINISHING: A PRACTICAL TREATISE ON MODERN METHODS OF FINISHING THE WOOD OF NEW BUILDINGS. By G. Whigelt. New York: Painters' Magazine. 1906. 124 pp. \$1.00.

LOGARITHMISCHE RECHENTAFELN FÜR CHEMIKER, PHARMAZEUTEN, MEDIZINER UND PHYSIKER. By F. W. Küster. Sixth edition Leipzig: Veit & Co. 1906. 99 pp. Marks 2.

HANDBUCH DER SEIFENFABRIKATION. By G. Deite. 1. Bd. Hausseifen und Textilseifen. Third edition. Berlin: J. Springer & Co. 1906. 12+633 pp. Marks 10.

THEORIE UND PRAXIS DER GARNFÄRBEREI MIT DEN AZO-ENTWICKLERN. By Dr Franz Erban. Berlin: J. Springer. 1906. 14+485 pp. Marks 12.

HANDBUCH DER BAUMWOLLE-INDUSTRIE. By Ernst Fränk. Berlin: Verlag für Textil-Industrie. 7+196 pp. Marks 5.

UEBER DIE DEDUKTION DER STOCHIOMETRISCHEN GESETZE. By Carl Benedicks. (Berlin: R. Friedlander & Sohn.) 1906. 14 pp. Mark 0.80.

GRUNDRISS EINER ENTWICKLUNGSGESCHICHTE DER CHEMISCHEN ATOMISTIK ZUGLEICH EINFÜHRUNG IN DAS STUDIUM DER GESCHICHTE DER CHEMIE. By Rich. Ehrenfeld. Heidelberg: C. Winter. 1906. 8+314 pp. Marks 8.

LEHRBUCH DER CHEMIE. AUTORIS DEUTSCHE AUSG. LEHRBUCH DER UNORGANISCHE CHEMIE FÜR STUDIERENDE. By A. F. Holleman. Fourth edition. Leipzig: Veit & Co. 1906. 12+451 pp. Marks 10.

CHEMISCHE PRAKTIKUM FÜR NATURWISSENSCHAFTLER. By M. Dittrich. Heidelberg: C. Winter. Marks 4.50.

HANDBUCH DER FARBEN-FABRIKATION. LEHRBUCH DER FABRIKATION. By George Zerr and R. Rubencamp. Dresden: Steinkopff & Springer. 1906. 12+850 pp. Marks 27.

MANUAL OF TOILET SOAP-MAKING. By C. Deite. New York: D. Van Nostrand Co. 1906. 147 pp. \$5.00.

CHEMISTRY OF PAINT AND PAINT VEHICLES. By Clare H. Hall. New York: D. Van Nostrand Co. 1906. 115 pp. \$2.00.

CHEMISTRY SIMPLIFIED. By G. A. Koenig. Phila: D. Van Nostrand Co. 430 pp. \$2.25.

NOTES ON VOLUMETRIC ANALYSIS. By J. B. Russell. New edition. New York: Dutton & Co. 1906. 8+94 pp. \$0.30.

FOOD INSPECTOR'S HANDBOOK. By Francis Vacher. Fourth edition. New York: D. Van Nostrand Co. 1905. 16+231 pp. \$1.50.

CHEMISCHE UND PHYSIKALISCH-CHEMISCHE UNTERSUCHUNG DER LINDENQUELLE ZU BIRRESBORN IN DIE EIFEL. NEBST UNTERSUCHUNG ÜBER DEREN RADIOAKTIVITÄT. By Ernst Hintz. Wiesbaden: C. W. Kreidel. 1906. 45 pp. Marks 1.20.

CHEMISCHE UND PHYSIKALISCH-CHEMISCHE UNTERSUCHUNG DER SALZTRINK

QUELLE ZU BAD PYRMONT. By Ernst Hintz. Wiesbaden: C. W. Kreidel. 1905. 45 pp. Marks 1.20.

KUNZES REPERTORIUM DER ORGANISCHEN CHEMIE. By K. Dammann. Freiberg i/B. Herder. Marks 4.

ANALYSE CHIMIQUE INDUSTRIELLE. By G. Lunge. Trans. by E. Campagne. Tome 1, Industrie minérales. Paris: Ch. Béranger. 640 pp. 22 fr. 50.

L'OXYGÈNE ET L'OZONE. LES ACIDES MINÉRAUX, L'AMMONIAQUE, LES VITRIOLS, LES ALUMS. By H. Pecheux. Paris: J. B. Baillière et fils. 96 pp. 1 fr. 50.

LES NOUVEAUTÉS CHIMIQUES POUR 1906. By Poulenc. Paris: J. B. Baillière et fils. 314 pp. 4 fr.

INTRODUCTION TO CHEMICAL CRYSTALLOGRAPHY. By P. Groth. Trans. by Hugh Marshall. London: Gurney. 1906. 136 pp. 4/.

BERICHT DER INTERNATIONALEN ANALYSEN-KOMMISSION AN DEM VI. INTERNATIONALEN KONGRESS F. ANGEWANDTE CHEMIE IN ROM, 1906. (IN DEUTSCHER, FRANZÖS. UND ENGL. SPRACHE.) By G. Lunge. Zurich: Zurcher & Furrer. 1906. 6+421 pp. Marks 10.

ANALYSE DES MÉTAUX PAR ELECTROLYSE. By A. Hollard and L. Bertiaux. Paris: Ch. Béranger. 184 pp. 6 fr.

QUALITATIVE BOTANISCHE ANALYSE DER DROGENPULVER. EINE EINFÜHRUNG IN DEN GANG EINE SYSTEMAT. MIKROSKOP. PULVERUNTERSUCHUNG. By P. Schürhoff. Berlin: J. Springer & Co. 1906. 6+9 pp. Marks 2.

ABRISS DER ALLGEMEINEN ODER PHYSIKALISCHEN CHEMIE. ALS EINFÜHRUNG IN DIE ANSCHAUUNGEN DER MODERNEN CHEMIE. By Carl Arnold. Second edition. Hamburg: L. Voss. 1906. 8+228 pp. Marks 3.75.

HANDBUCH DER ANGEWANDTEN PHYSIKALISCHEN CHEMIE IN EINZELDARSTELLUNGEN. \*3. Bd. MASCHINENKUNDE FÜR CHEMIKER. By Reg.-R. Ihering. \*\*4. Bd. Theorie der Verdampfung. By J. P. Kuenen. Leipzig: J. A. Barth. 1906. 8+396: 12+244 pp. \*Marks 15. \*\*Marks 13.

ELEKTROLYSE GESCHMOLZENER SALZE. By Richard Lorenz. 3. Thl. Elektromotorische Kraft. Halle: W. Knapp. 1906. 18+322 pp. Marks 10.

TECHNOLOGIE DER PAPIERFABRIKATION. By Eduard Engländer. Wien: Deuticke. 1906. 54 pp. Marks 1.

PRINCIPES DE CHIMIE. NOMENCLATURE, NOTATION ATOMIQUE. By H. G. Bonnin. Tours: Author. 32 pp. 1 fr.

CHEMISTRY OF HAT MANUFACTURING. LECTURES DELIVERED BEFORE THE HAT MANUFACTURERS' ASSOCIATION. By W. Smith. London: Scott, Greenwood. 1906. 132 pp. 7/6.

PRACTICUM DER PHYSIOLOGISCHEN UND PATHOLOGISCHEN CHEMIE NEBST ANLEITUNG ZUR ANORGANISCHEN ANALYSE FÜR MEDICINER. By E. Salkowski. Third edition. Berlin: A. Hirschwald. 1906. 13+315 pp. Marks 8.

SPÉKTROSKOPISCHE UNTERSUCHUNG DER TERBIUMPRÄPARATE V. DR. G. URBAIN. By G. Eberhard. Berlin: G. Reimer. 1906. 21 pp. Mark 1.

BEITRAG ZUR STEREOCHEMIE DER 2,5-DIKETOPIPERAZINE. By Emil Fischer und Karl Raske. Berlin: G. Reimer. 1906. 13 pp. Mark 60.

ANILINFARBEN UND IHRE FABRIKATION. By K. Heumann. IV. Thl. Hrsg. von Gust. Schultz. 2. Hälfte. 2. Abthlgn. Braunschweig: F. Vieweg & Sohn. 1906. 7,5 und pp. 1041-2595. Marks 50. Geb. Marks 56.

LIST OF BOOKS ON CERAMICS. Free Public Library of the City of Trenton, N. J.

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## THE LIME-SILICA SERIES OF MINERALS.<sup>1</sup>

BY ARTHUR L. DAY AND E. S. SHEPHERD.

Received July 15, 1906.

ANY ONE who has followed the work of the eminent Norwegian scientist, Prof. J. H. L. Vogt, during the past three or four years, must realize that an extraordinarily effective weapon has come into the service of petrology, the full power of which cannot at once be understood or appreciated. We refer to the methods and established generalizations of physical chemistry. The older science of chemistry has made such strides under these new theories of solutions that we really have little more to do than to apply them ready-made to our own problems, like a smooth and powerful machine tool of guaranteed effectiveness. Mineral solutions are after all only chemical solutions over again with slightly different components and a different, a very different range of temperatures and pressures.

It has been the purpose of this laboratory to attempt this task by a direct application of the principles and methods of quantitative physics and chemistry, or, in a word, to study mineral and rock formation by direct measurement at the temperatures where the minerals combine and separate like the solutions of ordinary chemistry under ordinary conditions. We further determined, wherever possible, to prepare chemically pure minerals for this purpose in order that such conclusions as we might reach should not be dependent upon dangerous assumptions regarding

<sup>1</sup> An extract from a paper of the same title read before the American Chemical Society at Ithaca, June 28, 1906.

the harmless character of the 5 or 10 per cent. of "impurities" not infrequently present in hand specimens from natural sources. It is at once obvious that in order to succeed the first experiments must be restricted to the simplest reactions and that these will not always be the most important or the most interesting, but the results will always be in definite terms and final when the materials used are pure. Furthermore, the accumulated experience obtained from simple cases will safely and surely lead to successful methods of a scope to meet the more complicated problems of rock formation.

This plan was really entered upon several years ago in a very small way and with very limited resources. The first paper,<sup>1</sup> which was published in 1904-5, contained a laboratory study of a typical isomorphous pair, the soda-lime feldspar series, carried out in the spirit of the above plan. The second,<sup>2</sup> which appeared in February of the present year, was a very careful study of enantiotropic mineral inversion between the mineral wollastonite and the pseudohexagonal form which has been obtained by several observers but which appears not to have been found in nature. The present paper, which is the third of the mineralogical series, undertakes to carry through a fairly complete set of measurements upon a typical eutectic pair—the lime-silica series. It is still incomplete in some particulars, notably at the ends of the series. Mixtures very rich in lime possess temperature constants which are beyond the reach of existing apparatus, while on the silica side the extreme viscosity and consequent inertness which were encountered in the soda feldspars effectually veil or prevent the development of the phenomena which occur there. Some approximate measurements have been made even in these regions (represented by dotted lines in the diagram, Fig. 2), but they have not the same accuracy as those portions of the curve which are represented by full lines. All the mixtures used were prepared with the greatest care and were chemically pure within one or two tenths of 1 per cent.

*Lime-Silica Minerals.*—In the lime-silica series only one well-defined mineral is known—wollastonite, which when melted

<sup>1</sup> Arthur L. Day, E. T. Allen and J. P. Iddings: *Am. J. Sci.* 19, 93 (1905). Publications of the Carnegie Institution of Washington, No. 31 (1905).

<sup>2</sup> E. T. Allen, W. P. White and Fred Eugene Wright: "On Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasilicate," *Am. J. Sci.* 21, 89 (1906).

usually crystallizes in a pseudohexagonal form of the same composition. This mineral has already been carefully studied by Allen and White, and the relation between the natural mineral and its second crystal form thoroughly cleared up. Pursuing the conventional methods of reasoning, we might also expect to have an intermediate mineral for the trisilicic acid,  $2\text{CaO} \cdot 3\text{SiO}_2$ ; an åkermanite analogue,  $4\text{CaO} \cdot 3\text{SiO}_2$ ; an orthosilicate,  $2\text{CaO} \cdot \text{SiO}_2$ ; and a tricalcium silicate,  $3\text{CaO} \cdot \text{SiO}_2$ . All of these minerals are deducible from the various silicic acids. We have undertaken to prepare and study the entire series of mixtures of lime and silica.

*Boudouard's Measurements.*—So far as known there has been only one serious attempt to determine the constitution of this series of minerals.<sup>1</sup> According to Boudouard, the freezing-point curve for the lime-silica minerals consists of four eutectics and three maxima (compounds), the maxima corresponding to the metasilicate, the orthosilicate and the tricalcium silicate. Unfortunately, the method used by Boudouard was a very inaccurate one. He prepared small cones of the various mixtures and placed these in a furnace alongside of Seger cones. The furnace was then heated and allowed to cool down again, after which the crucible was opened and the cone observed to see whether or not the mineral had melted. It is a common method in industrial practice, but has rarely been thought accurate enough for original determinations.

This method is peculiarly unsuited for such investigations for several reasons: Suppose the mixture to contain an eutectic with a greater or less excess of one of the components. The cone would begin to weaken as soon as the eutectic began to melt, and its further progress would be governed entirely by the relative quantity of eutectic present and its viscosity *after melting*. No information whatever regarding inversions in the solid or of the component in excess could be obtained, and errors of more than  $500^\circ$  would certainly occur (in fact did occur in Boudouard's case) in the interpretation of the softening temperature in some parts of the lime-silica curve. Let us illustrate by a perfectly obvious hypothetical case (Fig. 1): Assume first that the freezing-points change rapidly following a steep liquidus *AB* (see also Fig. 2, Curve *DE*). The amount of eutectic in concentrations *X* and *Y* will be so great as to soften the cone long before the

<sup>1</sup> Boudouard: J. Iron and Steel Inst., 1905, p. 339.

freezing-points  $Z$  and  $W$  are reached. If, on the other hand, the liquidus slopes gently ( $AC$ ), the amount of liquid eutectic as compared with the solid phase is smaller and the temperature of softening of the cone will approximate more closely to the change in freezing-point.

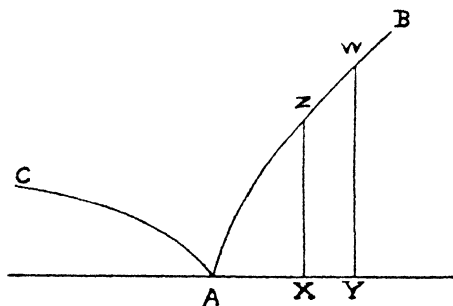


Fig. 1

Furthermore, if the cones are made up from the initial components ( $\text{CaCO}_3$  and  $\text{SiO}_2$  for example), the heat of combination is liberated as the cone approaches the melting temperature and raises the temperature of the cone above that of the furnace, producing sudden fusion, of which the neighboring Seger cone can receive no record.

Incidentally, one finds here the explanation of Hoffmann's experiments<sup>1</sup> on the temperature of formation of slags. Contrary to his statement that the "temperature of formation is above the temperature of fusion," just the reverse is true. Under normal conditions these mineral combinations occur at temperatures lower than the melting-point, the exceptions occurring only when the materials are so coarsely ground or poorly mixed that combination is retarded until the melting-point of the slag is passed. The orthosilicate of calcium is a very good instance of the formation of a compound below its melting temperature. We shall show later that while this compound melts at about  $2080^\circ$ , it is possible to prepare it below the melting-point of platinum, in fact in platinum vessels, by heating the finely ground material in the Fletcher furnace, regrinding, mixing, and reheating. By this process it is possible to obtain a compound which gives the optical tests for the orthosilicate and is entirely without free lime or silica.

<sup>1</sup> H. O. Hoffmann: Trans. Amer. Inst. Min. Eng. 29, 682 (1899).

Apart from the criticism which this particular application of cones appears to us to deserve, it is also well-known that the time factor is always very important in dealing with a Seger cone. Boudouard himself states (p. 343): "A very small difference in temperature or a *few minutes' additional heating*<sup>1</sup> often suffices for the softening stage to pass into one of complete fusion." If this statement was made understandingly, the method merited rejection by Boudouard himself. Furthermore, the use of Seger cones for exact work will always be unsatisfactory because it depends upon the judgment of the operator to say when a cone has "fallen" sufficiently to be considered melted, and different observers almost always obtain widely different results under like conditions. As has been pointed out by Day and Allen,<sup>2</sup> any method of measurement which is not based upon some reasonably sharp physical change must be expected to give different results in different hands. Suppose this method were to be applied, for example, to the determination of the melting temperature of orthoclase or albite, or even pure quartz, which have been shown to possess a viscosity entirely comparable in magnitude with the rigidity of the solid crystalline mineral; almost any conclusion could have been reached under these conditions.

It is stated by M. Boudouard that all mixtures of lime and silica between 30 and 90 per cent. of lime melt below 1500°. This certainly cannot be the case. Pure orthosilicate of calcium when heated in a platinum crucible will stand without showing the slightest trace of melting while the platinum containing vessel melts down. The temperature must therefore be at least as high as the fusion point of platinum (1720°). We found no lime-silica mixtures richer than 60 per cent. in lime which could be melted in platinum vessels.

Apart from the uncertainty in the temperature measurements offered by Boudouard, we shall also undertake to show in its proper place that there is no pure lime-silica compound corresponding to tricalcium silicate. We are therefore somewhat at a loss to explain in any satisfactory way how the published curve which has attracted so much attention in England, was really obtained.

In this kind of investigation it is always desirable to begin with

<sup>1</sup> Italics are ours.

<sup>2</sup> Loc. cit.



a careful determination of the physical properties of the pure components, although in the present case it must be admitted that this was the most inaccessible and difficult portion of the field over which we worked.

*Lime.*—Calcium oxide melts at a temperature so high that it is not yet possible to make a satisfactory determination of its melting-point. It can be fused in the electric arc under favorable conditions to a clear liquid of low viscosity which crystallizes readily into a well developed cubic structure. Near its fusing temperature, lime either becomes quite volatile or the carbon of the arc reduces it to the metal which volatilizes and is immediately reoxidized outside of the heated zone. We are unable to offer conclusive evidence in favor of the one hypothesis or the other, but the fact that pure lime at  $2000^{\circ}$  shows no signs of a high vapor pressure points rather to the second explanation as the correct one.

For experiments with lime fusion, we obtained some artificial graphite,<sup>1</sup> practically free from all impurities, so that no contaminating substance was introduced into the fused lime from the electrodes. To further guard against possible contamination, only that part of the cake which formed above the (horizontal) arc was used in determining its physical properties.

*Density of Lime.*—The density of fused calcium oxide was determined as follows: A selected portion of the crystalline mass was finely ground, ignited to drive off adsorbed water, and weighed in carefully dried turpentine after the method of Day and Allen. The results are not in very good agreement, due to the difficulty of weighing out the product without its becoming superficially hydrated or absorbing carbon dioxide.

Fused CaO.  $H_2O$  at  $25^{\circ} = 1$ .

3.313

3.307

3.329

Mean density, 3.316 ( $25^{\circ}$ )

This crystallized lime is much less readily attacked by water than is the amorphous oxide. It is, however, not indifferent to water. Five grams of the crystals when ground and mixed with a small quantity of water in a test-tube scarcely raised the tempera-

<sup>1</sup> Prepared especially for us by the International Acheson Graphite Company, Niagara Falls, N. Y.

ture at all, but upon standing for some five minutes, the charge exploded with considerable violence. Unpowdered blocks of the crystalline oxide when placed in cold water dissolved slowly without appreciable heating. Hot water attacks them more rapidly, but the action of the water is slow in both cases when compared with the amorphous lime.

The hardness, according to Mohr's scale, is between 3 and 4.

*Silica*.—The melting temperature of silica has been variously estimated from 1200° to 2000°, but so far as known no careful determination of it has ever been made. Since this oxide melts to an extremely viscous liquid, attempts to determine the melting temperature by observing the softening of the charge are wholly misleading. The molecular deorientation proceeds very slowly, extending over a considerable range of temperature, as albite and orthoclase have been found to do,<sup>1</sup> but with the disadvantage that this temperature region is too high to be reached with a thermoelement and no other method of temperature measurement possesses sufficient sensitiveness in this region to locate the melting temperature by the heat absorbed during slow fusion. Determinations of the freezing-point are out of the question, owing to the inertness of the viscous melt.

An approximate determination of the melting temperature was made in this way: A gram or two of finely powdered quartz was placed in a small iridium crucible and heated in an iridium tube furnace.<sup>2</sup> Experience has shown that melting and inversion phenomena in very viscous substances take place much more readily if the material is finely divided. A tiny fragment of platinum foil was then laid on the top of the charge and the furnace slowly heated until the foil was observed to melt. Upon removing the charge from the furnace and examining it microscopically, evidence of fusion was found throughout the mass. The crystal grains had inverted to tridymite and the superficial liquefaction had caused them to sinter tightly together, but no displacement of the grains had taken place. At the temperature of melting platinum, therefore (1720°), silica shows positive evidence of fusion. Other similar charges were then prepared

<sup>1</sup> Day and Allen: Loc. cit.

<sup>2</sup> No detailed description of the apparatus used or the methods of operating it can be included in this brief abstract. They are nearly all accessible in other publications from this laboratory or in contemporary pyrometric literature.

and the operation repeated with longer exposures and temperatures slightly below the melting-point of platinum, the temperatures being measured with a Holborn-Kurlbaum optical pyrometer<sup>1</sup> focused on the platinum fragment. By repeating this process at short temperature intervals and with about twenty minutes' exposure, melting was definitely established as low as 1625°.

The iridium furnace is unfortunately not adapted for long-continued heating, and the platinum coil furnace will not reach this temperature, so that an effort to discover a definite temperature below which the solid is stable and above which it will melt, if given time enough, was abandoned. If the heating is moderately rapid, the crystalline solid will persist far above the melting-point of platinum; if slow enough, it liquefies completely at 1625° or even lower. It is probably a fair assumption that pure crystalline silica begins to melt at about 1600°,<sup>2</sup> and will continue to complete fusion, if given time enough—above that point the higher the temperature the more rapid the melting. A charge of quartz was heated for a long time in a platinum furnace at 1550° without producing a trace of fusion.

There is little satisfaction in pursuing an inquiry of this kind. As has been stated elsewhere with reference to an entirely similar case,<sup>3</sup> the term "melting-point" does not appear to be well applied to cases of this character in which the crystalline structure persists for days or weeks at temperatures above the point where melting begins. If the change of state is to be defined by the

<sup>1</sup> Holborn and Kurlbaum: *Ann. Physik.* 10, 225 (1903).

<sup>2</sup> In a recent number of this *Journal* (July) Mr. Alexander Lampen publishes an experimental determination of the melting-point of a "piece of pure quartz" as follows (five minutes exposure):

Edges rounded.....	1650°
Fused .....	1700°

Our experience inclines us to the belief that these temperatures are too low for the stages of the melting described for two reasons: (1) We found no crystalline quartz fragment upon which rounded edges could be observed from without the furnace after five minutes' heating even at the temperature of melting platinum (1720°), a fixed point in which great confidence can be placed; (2) if Mr. Lampen was able clearly to see incipient melting through red glass within his furnace, as he has stated, the radiation which he measured cannot have been "black" and his instrument *must* have read too low.

This note is added by request since the reading of the paper.—THE AUTHORS.

<sup>3</sup> Publication 31, Carnegie Institution of Washington, p. 74 (3).

absorption of heat, and the absorption of heat extends over a wide range of temperatures and conditions, our forms of expression should be revised somewhat to include these hitherto unrecognized cases.

*Tridymite*.—The relation between tridymite and quartz appears to be a simple one, although the literature of the subject is unsatisfactory. But few trustworthy observations have been recorded and the conclusions drawn from them are vague and contradictory. So far as known, quartz has never been crystallized as such from mineral fusions except where catalyzers were present. Tridymite has probably been obtained by several individuals through the accidental crystallization of fused silica vessels,<sup>1</sup> but no especial attention appears to have been given to the circumstances in which it occurs, and its identification has not always been positive.

Like the melting temperature, the inversion of quartz to tridymite and the recrystallization of fused silica are very difficult phenomena to study, owing to the extreme inertness of the material, but a number of experiments have been successfully carried out which appear to clear up the situation, even though the inversion temperature cannot be determined with any great accuracy.

First of all, we heated a large charge of finely ground quartz and followed the temperature curve carefully from 400° to 1600°. It was found after the experiment that the quartz crystals had, for the most part, gone over into tridymite and the change in the volume accompanying the inversion had generated enough pressure to completely shatter the open platinum crucible which contained the charge. The change was so gradual, however, that no record of it appeared upon the thermal curve. Subsequent experiments in which we endeavored to change crystalline quartz into tridymite at lower temperatures were successful as far down

<sup>1</sup> Prof. Dr. L. Holborn, of the Physikalisch-technische Reichsanstalt, Dr. M. Herschkowitsch, of the firm of Carl Zeiss in Jena, Dr. Küch, of the firm of Heraeus in Hanau, and the Rev. Theodor Wulf, S. J., formerly of Göttingen, in the preparation and use of quartz glass vessels, have noticed that the glass devitrifies at high temperatures in the presence of water vapor or after long usage. So far as we are aware, all of these observations have remained unpublished. Hahn, in the *Int. Cong. f. angewandte Chemie*, Berlin, 1903 (Vol. I, p. 714), notes the devitrification of a quartz glass tube at 1100°. He also identified the crystal formation under the microscope as tridymite.

as  $1100^{\circ}$ . To be sure, entire crystals showed no change whatever after six hours' exposure at  $1400^{\circ}$ , but powdered quartz is completely changed into tridymite after a few hours at that temperature. On the other hand, if finely divided amorphous silica, *i. e.*, fused ("quartz glass"), or better, precipitated silica, be allowed to remain for a short time at any temperature above  $1000^{\circ}$ , it changes promptly to tridymite—the precipitated material very rapidly, the quartz glass much more slowly. Neither the glass nor the precipitated silica ever crystallized as quartz at temperatures above  $1000^{\circ}$ , nor is there any difference in the optical properties of the tridymite obtained at the different temperatures, either from the quartz crystals or the amorphous silica. The rate of change is much influenced by the fineness of the powder, although there is no difficulty in crystallizing large blocks of solid quartz glass at the higher temperatures. In our experiments in the preparation of quartz glass,<sup>1</sup> we frequently obtained isolated spherulites of tridymite several millimeters in diameter, even with rapid cooling, which appeared to have been started by a grain of graphite or carborundum powder accidentally falling into the melt. On one occasion the entire block was coated with tridymite to a depth of a millimeter or more.

We have therefore succeeded, by direct experiment upon pure silica, in establishing the fact that tridymite, and not quartz, is the stable crystalline form of silica for all temperatures above  $1000^{\circ}$ .

At lower temperatures than this it is impossible, in view of the inertness of the substance, to obtain any further reaction, even with the finest precipitated silica, within the time available for a laboratory experiment. A month's exposure at  $900^{\circ}$  produced no change. We therefore followed the example of several distinguished predecessors in this field, and tried various catalyzers.

*Formation of Quartz.*—Hautefeuille thought he had produced quartz crystals by fusing amorphous silica with sodium tungstate at  $900^{\circ}$ , but the methods of high temperature measurement commonly employed in his time were very imperfect, and the temperature is undoubtedly too high. He has also stated that he obtained it by fusion with lithium chloride. Both Hautefeuille and Margotet have recorded the fact that in the presence of lithium chloride amorphous silica changes to tridymite at high

<sup>1</sup> Day and Shepherd, "Quartz Glass," *Science*, 23, 670 (1906).

temperatures and to quartz at low temperatures. We obtained quartz crystals from glass by the use of 80 per cent. potassium chloride and 20 per cent. lithium chloride, at all temperatures below  $760^{\circ}$ , while at temperatures of  $800^{\circ}$  and higher, only tridymite crystals appeared. The same results were obtained with vanadic acid and with sodium tungstate. The inversion point

quartz  $\rightleftharpoons$  tridymite

therefore occurs at about  $800^{\circ}$ . This conclusion is subject to the assumption that the inversion temperature is not lowered by the catalyzing agent—an assumption which seems to be justified by the fact that the quartz crystals obtained in this way (judged by the optical properties) appear to hold none of the reagent in solid solution.

The situation is, then, briefly this: Both quartz and amorphous silica at high temperatures change to tridymite. Quartz is consequently the unstable form of silica from  $800^{\circ}$  upward, and will go over into tridymite whenever conditions favorable to the change are present. The melting temperature of silica is therefore properly the melting temperature of tridymite and not of quartz as it is commonly described. We have once or twice succeeded, by extremely rapid heating, in melting quartz as such, or more correctly speaking, in carrying a quartz charge past the melting temperature of tridymite, melting a portion of it and finding a residue of quartz afterward which had neither inverted nor melted. It would hardly be possible by any known method, however, to obtain a separate melting temperature for quartz independently of tridymite.

The reverse operation, showing that tridymite inverts to quartz at temperatures below  $760^{\circ}$ , cannot be carried out in the laboratory without the use of catalyzers on account of the extreme slowness of the change. In the presence of 80 per cent. potassium chloride and 20 per cent. lithium chloride, quartz begins to appear from tridymite in quantities sufficient for positive identification after an exposure of five or six days at about  $750^{\circ}$ . No effort was made to invert the entire charge, on account of the slowness of the change and the fact that its character was now fully established. The glass crystallizes to quartz below  $760^{\circ}$  and to tridymite above  $800^{\circ}$ ; crystalline quartz goes over to tridymite above  $800^{\circ}$ , and tridymite to quartz at  $750^{\circ}$ ; the change is therefore enantiotropic and not monotropic. •

Incidentally, a sufficient reason has been given for the complete failure of experimenters to produce quartz without catalysis. If dry silica at  $900^{\circ}$  is so inert as to undergo no reaction at all during a month's exposure under favorable conditions, how can we expect reaction below  $800^{\circ}$  where the viscosity is even greater? Silica must be crystallized below  $800^{\circ}$  to produce quartz.

*Density of Silica.*—The density of the quartz used and obtained in our experiments was determined with the following result, the aggregate impurity being not over one-tenth of 1 per cent.

Purified natural quartz.	Quartz glass.	H <sub>2</sub> O at $25^{\circ}$ = 1.
2.655	First preparation .....	2.209
2.653	" " .....	2.215
2.654	" " .....	2.212
	Second " .....	2.213
	" " .....	2.215
<hr/> Mean, 2.654 ( $25^{\circ}$ )		<hr/> Mean, 2.213 ( $25^{\circ}$ )

It will be noted that there is a difference of more than 16 per cent. between the density of the glass and that of the quartz crystals.

A charge of powdered crystalline quartz heated for several days at  $1200^{\circ}$  appeared under the microscope to be homogeneous tridymite. Some observations of its density are contained in the subjoined table under the heading "tridymite from quartz." A similar charge obtained by crystallizing the glass at  $1200^{\circ}$  (three days) also showed no residual glass under the microscope. Its density is given under the heading "tridymite from glass." A second table contains confirmatory measurements upon a second preparation heated to a slightly different temperature.

First preparation ( $1200^{\circ}$ ).		Tridymite (H <sub>2</sub> O at $25^{\circ}$ = 1).	
From quartz.	From glass.	Second preparation (6 days at $1160^{\circ}$ ).	
		From quartz. <sup>1</sup>	From glass.
2.325	2.316	2.327	2.319
2.330	2.318	2.325	2.318
2.325	2.316		2.316
	2.319		

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Mean, 2.326 ( $25^{\circ}$ )    

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Mean, 2.317 ( $25^{\circ}$ )    

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Mean, 2.326 ( $25^{\circ}$ )    

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Mean, 2.318 ( $25^{\circ}$ )

Whether the quartz had not completely changed to tridymite, or the glass was incompletely crystallized, or perhaps both, is of little moment. It is a very slow change and the agreement between the values obtained by the two methods is sufficiently

<sup>1</sup> This preparation was afterward found to contain some unchanged quartz.

good, when considered in the light of their identical optical properties, to establish the absolute identity of the tridymite formed from the glass and from the quartz crystals.

*The Lime-Silica Series.*—Having determined the properties of our two component minerals, we are prepared to enter upon the study of their relation to each other in mixtures of various proportions. It will be borne in mind that inasmuch as we found no proper melting-point for pure silica on account of the inertness (if we may so describe it) with which it resists molecular de-orientation when heated, so compositions which are immediately adjacent to the silica end of the series may be expected to show the same property and to yield but little information from a direct application of the usual pyrometric methods. Similarly, pure calcium oxide and its immediate neighbors are well out of reach of accurate measurement by any existing pyrometers. But even without these important measurements, we have been able to obtain sufficient information in the more inaccessible portions of the curve to enable us to describe all the reactions involved with little probability of error. Inasmuch as lime is probably the most refractory mineral known, it will require no apology if we simply leave its thermal constants until greater perfection in pyrometric measurements shall have been attained.

*Preliminary Orientation.*—Given chemically pure and *well mixed* (by grinding and *repeated melting*) preparations, it is not a difficult matter to secure a preliminary survey of a field of this kind. The mineral wollastonite is known, and more than that, is known to possess a melting temperature lower than either lime or silica. There is, therefore, immediate reason for anticipating eutectic relations somewhere in the series. If wollastonite forms a eutectic with components on one or both sides of it, mixtures containing slightly more lime or slightly more silica than wollastonite will have lower melting temperatures than it. A simple and effective mode of preliminary procedure is therefore to take a tiny pinch of a number of the percentage mixtures adjacent to wollastonite, place them in order upon a narrow platinum ribbon which can be heated electrically to uniform brightness, and observe the order in which they melt. No temperature measurement is worth while; the information obtained can only serve for orientation and must be verified by more reliable pyrometric methods.



If a eutectic is present on either side of the compound, it will be the first to melt, and the compound last; the intermediate mixtures are not important. If the materials are not too viscous the melting will be sharp and the material will crystallize again on slow cooling. A few repetitions, or the introduction of intermediate compositions in doubtful cases, will usually enable a preliminary curve to be drawn in which the compounds and eutectics which are within reach will be correctly located. In fact, for many substances they can be very exactly located in this way; intermediate compositions, on the other hand, may be very misleading, depending upon the behavior of the eutectic present after the melting temperature of the latter has been passed.

Proceeding in this way, a eutectic will be readily located between silica and wollastonite at the composition 63 per cent.  $\text{SiO}_2$ , 37 per cent.  $\text{CaO}$ , and another on the other side of wollastonite at the composition 46 per cent.  $\text{SiO}_2$ , 54 per cent.  $\text{CaO}$ . We will allow the other component of this second eutectic to remain unidentified for the moment, as no stable lime-silica mineral richer in lime than wollastonite is known. If we continue our platinum ribbon experiment with continually increasing percentages of lime, we shall find that after one or two steps beyond this second eutectic the platinum ribbon will burn out without melting the little grains. In other words, the melting temperature of lime-silica mixtures richer in lime than 60 per cent. are all higher than that of platinum. To meet this difficulty, we substituted iridium for platinum ribbon, and proceeded as before laying out a whole series of compositions from 60 per cent.  $\text{CaO}$  on. We soon discovered a third and very sharp eutectic with the composition  $67\frac{1}{2}$  per cent.  $\text{CaO}$ ,  $32\frac{1}{2}$  per cent.  $\text{SiO}_2$ , and a maximum indicating a probable compound at 65 per cent.  $\text{CaO}$ , 35 per cent.  $\text{SiO}_2$ , which corresponds to the anticipated orthosilicate. No other points were obtained up to  $2100^\circ$ .

Thus in a very short time and in this simple and expeditious way we were able to locate three eutectics (37, 54 and  $67\frac{1}{2}$  per cent.  $\text{CaO}$ ) and two compounds (48 and 65 per cent.  $\text{CaO}$ ) between lime and silica, canvassing for the purpose practically all the compositions from pure lime to pure silica at intervals of 1 or  $2\frac{1}{2}$  per cent. and all temperatures from  $500^\circ$  to  $2100^\circ$ . Beyond 75 per cent. lime and below 32.5 per cent. the method yields no informa-

tion for reasons which have been elaborated elsewhere. All the important determinations were verified by numerous repetitions.

If we now compare the compounds obtained by this preliminary investigation with those which we were led to anticipate from Boudouard's observations, as well as from the hypothetical silicic acids, we find that we have located two—the metasilicate and orthosilicate—and missed two—the åkermanite analogue ( $4\text{CaO} \cdot 3\text{SiO}_2$ ) and the tricalcium silicate. The next step was therefore obviously to bring all our resources to bear upon these particular compositions in order definitely to ascertain whether such compounds can exist when the components are pure, and if so, under what conditions and with what properties. That we succeeded in reaching a positive conclusion upon this point is due in large measure to the skilful microscopic examinations by Mr. Fred Eugene Wright of this laboratory, of which a detailed record prepared by him will be found with the full text of this paper soon to be published.

*The Åkermanite Analogue.*—The åkermanite analogue ( $4\text{CaO} \cdot 3\text{SiO}_2$ ) was first taken up and the neighboring concentrations investigated at intervals of 1 per cent. with the greatest care. A large charge of this particular composition was repeatedly melted and examined under the microscope but it failed to show homogeneous structure or any characteristic property of a compound. On the other hand, the pseudo-wollastonite and the orthosilicate appeared in the proportion appropriate to its place in the series. Furthermore, since the melting temperatures of these mixtures were within the reach of our platinum furnaces, and therefore of our most sensitive pyrometric measurements, we were able to hold the temperature constant at any desired point and then by rapid cooling (quenching in mercury) to fix any phase which might have been present and become unstable below that temperature. Here again we found that pseudo-wollastonite and the calcium orthosilicate were the only phases which could be separated from this or any mixture of the pure components in the neighborhood. It is our belief, therefore, that the åkermanite mineral cannot exist between the pure components and is only possible when other substances are present. This is further indicated by the fact that the metasilicate of calcium in the presence of magnesium oxide forms a solid

solution of which the limiting concentrations are relatively wide and which would easily account for the åkermanite mineral produced from the fusion of the three components.

*The Orthosilicate of Calcium*,  $\text{Ca}_2\text{SiO}_4$  (65 per cent.  $\text{CaO}$ ).<sup>1</sup>—It has long been known that the orthosilicate of calcium, although not found in nature, can be formed by the fusion of the pure components. The temperature of fusion is very high and the crystalline material obtained disintegrates spontaneously at the lower temperatures. The cause of the disintegration has not been carefully studied heretofore, and optical determinations of it are difficult, owing to the extreme fineness of the disintegrated product. Our investigation establishes the fact that the orthosilicate of calcium can exist in three polymorphic forms which we have designated as  $\alpha$ ,  $\beta$  and  $\gamma$ , in the order in which they form from fusion. The  $\alpha$ -form is the only modification which is stable in contact with the melt. Its specific gravity is about 3.27, determined in methylene iodide solution upon fresh crystals. Its hardness is 5-6, Mohr's scale; crystal system, monoclinic.

Below  $1410^\circ$  the  $\alpha$ - changes into the  $\beta$ -form, of which the density, 3.28 (measured by comparing the indices of refraction), is but little different from that of the  $\alpha$ -modification. The substance was too unstable for determinations of the density to be made in the ordinary way. It crystallizes in the orthorhombic system. The inversion point between the  $\alpha$ - and  $\beta$ -varieties is well marked and distinguishable over almost the entire range of compositions of which the orthosilicate is a component, as indicated in the diagram (Fig. 2, line *MN*). The inversion of  $\beta$  into  $\gamma$  occurs at about  $675^\circ$  with a large increase of volume, which at once explains the disintegration of the material. The temperature at which this inversion occurs is somewhat variable, and it is not readily reversible. It is much too slow a change to admit of pyrometric determination, but it is possible to locate it approximately by quenching the material from selected temperatures in the neighborhood of the inversion point. The usual procedure was to take a small portion of the disintegrated material, fold it tightly between thin strips of platinum and place these in the furnace. The temperature was then raised to any chosen value

<sup>1</sup> The metasilicate of calcium has been made the subject of a special paper by Allen, White and Wright (loc. cit.), and will not receive detailed consideration here.

and maintained constant for periods of time varying from six hours to three or four days. At temperatures far enough removed from the inversion point, the transition from one form into the other was fairly rapid, but as the temperature of inversion approaches, equilibrium is attained with increasing difficulty. After the furnace had remained at this constant temperature for a length of time, it was opened, the platinum strips containing the orthosilicate were removed, and quickly plunged into mercury. In this way, from temperatures just above the inversion point, it was possible to fix the  $\beta$ -form long enough to allow of its optical determination.

The disintegration on cooling appeared to depend considerably upon whether or not the  $\alpha$ -form had first been allowed to change into the  $\beta$ -form. For example, if a small portion of the orthosilicate is fused before the oxyhydrogen blast and then plunged directly from the flame into mercury, the quenched material will usually be stable for a considerable time. If the flame is removed but a moment and the slightly cooled specimen plunged from white heat into mercury, disintegration is immediate. This phenomenon was further verified by fusing the material and dropping it into a furnace held at about  $1200^{\circ}$ . After a few moments the charge was then removed and quickly plunged into mercury. Treated in this way, all of  $\alpha$  goes over into  $\beta$ , which in turn will disintegrate completely with little or no delay after reaching the  $\beta \rightleftharpoons \gamma$  inversion temperature. One will sometimes get the  $\alpha$ -form by slow cooling, but never the  $\beta$ -form.

The  $\gamma$ -form of the orthosilicate crystallizes in the monoclinic system. Its density, determined in turpentine, by the pycnometer method, is

2.973

2.975

Mean, 2.974 ( $25^{\circ}$ )

The difference in volume between the  $\gamma$ - and  $\alpha$ - or  $\beta$ -forms is therefore nearly 10 per cent., and since the  $\alpha$ - and particularly the  $\beta$ -form goes over into the  $\gamma$  at low temperatures with the greatest readiness, the disintegration of the fused orthosilicate is readily explained.

Neighboring mixtures containing the orthosilicate as a component disintegrate beginning with compositions containing only 51 per cent. of lime. The disintegration of this preparation

is, however, very slow, and usually does not take place at all unless the mixture has been held for some time at a relatively high temperature. The 54 per cent. mixture can also be readily obtained without disintegration, but with more than 54 per cent. of lime, disintegration always occurs under the ordinary conditions of preparation.

If the orthosilicate be heated to temperatures only slightly above  $QR$  (Fig. 2) so as to produce the  $\beta$ -form without sintering, disintegration does not appear on cooling for the reason that the change in volume is not apparent in the powdered material. If the charge be heated to about  $1400^\circ$ , or above  $1410^\circ$  where the  $\alpha$ -modification appears, it sinters tightly together and the disintegration phenomenon is again observed. Charges sintered together at  $1400^\circ$  to  $1500^\circ$  and held continuously at any temperature above  $QR$  do not disintegrate so long as this temperature is maintained, but as soon as the temperature drops below  $QR$ , disintegration recurs, but not at a constant temperature nor at any characteristic rate, the change being very dependent upon the conditions obtaining at the time.

The orthosilicate is easily attacked by water, giving an alkaline reaction, even when the water is cold, while with boiling water it is possible to wash out as much as 10 per cent. of lime. This probably accounts for the absence of this mineral in nature. Ammonium chloride solution even when cold decomposes all the mixtures of lime and silica.

*The Tricalcium Silicate*,<sup>1</sup>  $3CaO, SiO_2$ .—This silicate owes its supposed existence mainly to those investigators who have found it necessary to postulate such a compound in order to explain the constitution of Portland cement. So far as the literature shows, no one has ever isolated and described a pure and homogeneous compound of this composition or defined its properties.<sup>2</sup> Many and varied attempts to make it have uniformly resulted in mixtures in which poor optical properties have made the conclusions insufficiently positive.<sup>3</sup>

<sup>1</sup> In the literature of the cement industry the hypothetical compound,  $3CaO, SiO_2$ , is almost universally referred to as the "tricalcic silicate." The substitution of "tricalcium silicate" in conformity with common chemical usage will of course cause no confusion.

<sup>2</sup> It is sometimes described as "nearly homogeneous."

<sup>3</sup> A moment's consideration should suggest that there is no real necessity for assuming the existence of the tricalcium silicate in order to explain

We began the investigation of this composition by fusing the components in the proper proportions and examining the fused product microscopically as others had done. Most previous investigators, however, appear to have depended for microscopic evidence upon the ordinary optical figures and interference colors. Now, it so happens that this mixture when fused crystallizes in an extremely fine structure in which the interference colors are quite different from those of the orthosilicate to be sure, but this is merely the result of the fine state of division and the overlapping of the crystals, and not to another compound. If one examines any of the compositions in which the tricalcium silicate might be expected to figure, using the very sensitive index of refraction as a test of homogeneity, he will find that in every preparation containing more lime than 65 per cent. (orthosilicate composition), there is an excess of free lime which can be positively identified. We have fused the tricalcium silicate composition, cooled it rapidly and slowly in various ways without once failing to find free lime present in quantity. Through the kindness of Dr. Clifford Richardson, we were also given an opportunity to examine some of the tricalcium silicate prepared and described by him, and while its ordinary appearance under the microscope differed from that of the orthosilicate, a study of the index of refraction showed the supposed tricalcium silicate to be a mixture of the orthosilicate with free lime. Having failed to obtain a single tricalcium silicate which did not contain free lime, and because every specimen which we examined, including many which had been prepared by others, also showed the orthosilicate to be present, we were forced to conclude that the tricalcium silicate has no real existence. We also tried fusing the tricalcium silicate composition with a flux, but the product was always the orthosilicate of calcium.

the nature of Portland cement. It is a system of at least three components with a great number of possibilities. The real difficulty appears to have been that crystallized lime is relatively inert and does not readily give the reactions common to ordinary lime, consequently the tests which were thought to demonstrate the absence of free lime in these preparations have proved very misleading. For example, we have found that crystals of lime are but very slowly attacked by water (see p. 1094). Another argument which is freely offered—that there can be no free lime present “because if free lime is added the cement dusts spontaneously,” is obvious fallacy. Free lime does not cause the dusting, and if it did the fact that the *addition* of free lime caused dusting would be no proof that none was present.

Although we are anticipating pyrometric studies which follow, a single glance at our diagram (Fig. 2) will show that we have found and measured the  $\beta \rightleftharpoons \alpha$ -inversion of the orthosilicate in all the compositions up to 90 per cent. lime which we could never have done with a tricalcium silicate intervening unless the tricalcium silicate be assumed to possess an identical inversion—which would be a rare coincidence. We have therefore complete optical and pyrometric evidence of the persistence of the orthosilicate throughout the supposed tricalcium silicate region, and no compound of tricalcium silicate composition can exist there.

By way of completing the search for hypothetical compounds, we also examined compositions corresponding to the trisilicic acid, but found that the mixtures of lime and silica from which the salt of this acid might be expected to crystallize did not give any new phases. These mixtures showed well developed pseudo-wollastonite with the tridymite eutectic, and neither rapid cooling nor crystallization of the glass at low temperatures gave any indication whatsoever of the hypothetical compound.

*The Temperature Constants.*—We have now definitely located the compounds of lime and silica which can exist between the pure components together with the eutectics which they form. It only remains to study their thermal properties somewhat more consistently by accurate pyrometric apparatus. It was not found possible to determine the presence of the eutectic (line *HBI*, Fig. 2) in the 10 and 20 per cent. compositions, for reasons which will have become sufficiently clear already, but the microscopic evidence shows the tridymite to be normal, whether it forms from pure silica or in the presence of lime, so that the eutectic must extend over to the silica axis. From 30 per cent. on there was no difficulty in observing it pyrometrically. Mean values of the observations obtained are included in Table I.

TABLE I.

(Line *HI*, Fig. 2.)

	Eutectic. Tridymite—pseudo-wollastonite.				
Percentage of CaO .....	30	32	35	40	45
Eutectic melts.....	1420°	1418°	1418°	1421°	1413°

The liquidus *AB* (Fig. 2) has been drawn as a dotted line. The value assumed for the melting temperature of silica is based upon considerations which have been elaborated elsewhere (p. 1095). It requires no further comment except perhaps to call

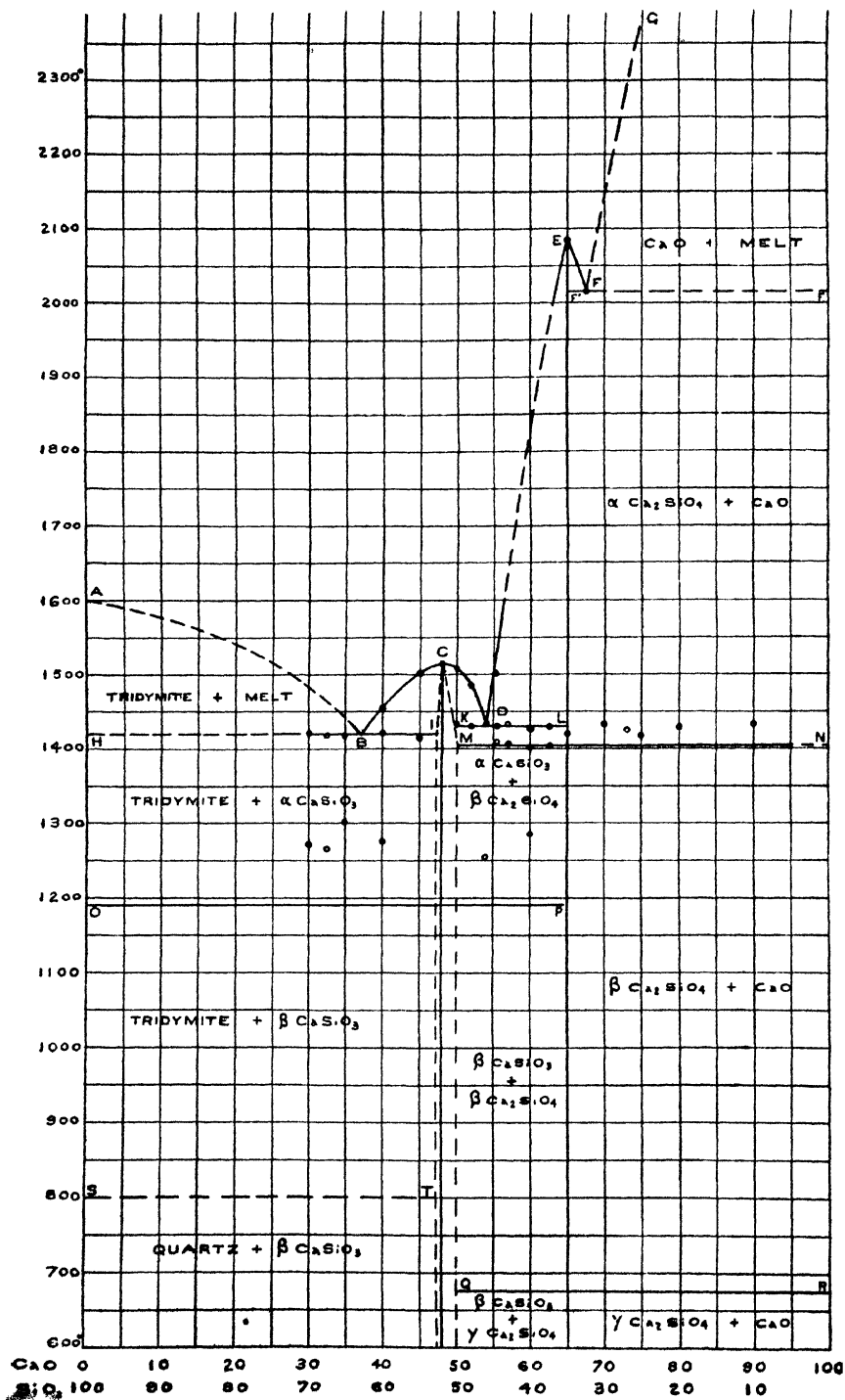
attention to the fact that it is much lower than the temperature usually assigned to it. As the mixtures grow richer in lime, the melting of the excess of silica seems to be considerably facilitated, but there are no points sufficiently sharp to serve any purpose as quantitative determinations until we reach the composition 30 per cent.  $\text{CaO}$ , 70 per cent.  $\text{SiO}_2$ . The microscopic evidence is, however, both satisfactory and sufficient as to the nature and continuity of the curve.

Along the branch *BC* (Fig. 2) of the liquidus, the pseudo-wollastonite is the solid phase. It crystallizes from these mixtures in laths between which an extremely fine-grained, almost sub-microscopic eutectic appears.

It may be remarked in passing that the "eutectic structure" in minerals is by no means so characteristic as in the case of the alloys. Owing to the great viscosity of these melts and consequent slowness of diffusion, it is evident that there is no opportunity for the formation of the characteristic grain structure which we have come to associate with the eutectics of the alloys. This almost complete absence of diffusion in silicate melts makes it necessary to proceed with great caution in applying to minerals the methods which are easily and effectively applied to the alloys. For example, in alloys it is possible to crystallize out a portion of the solid phase, then to separate the mother-liquor and by analysis of the two to determine the composition of the solid phase. In the case of mineral mixtures, the segregation of the eutectic is, for laboratory experiments at least, very indefinite. We have repeatedly examined different regions of a charge in which the eutectic was known to separate, in the hope of finding it segregated towards the middle of the charge, as commonly happens with alloys, but in no case were we able to detect more of the eutectic in one part of the charge than in another. It is usually finely divided and intimately mixed with the primary crystals.

The properties of the pseudo-wollastonite which separates along the branch *BC* are not quite identical with those of the compound when prepared pure, from which it is evident that a certain amount of silica must be taken up by it in solid solution. The amount thus held in solution is certainly less than 2 per cent., but its exact determination microscopically is very difficult indeed. Furthermore, this pseudo-wollastonite when changed to





wollastonite still shows a slightly different optical character from the pure material, showing that the solid solution apparently continues after the inversion. For brevity, the pseudo-wollastonite has been designated  $\alpha$ -CaSiO<sub>3</sub>, and wollastonite  $\beta$ -CaSiO<sub>3</sub>, in (Fig. 2). The branch of the liquidus *CD* was readily determined, as well as the beginning of the branch *DE*. It was not possible, however, to follow the branch *DE* beyond 57 per cent. owing to the steepness of the curve, which rapidly carries it out of the range of the accurate thermoelectric methods.

Mean values of the observations along the curve of melting-points are continued in Table II.

TABLE II.  
(Curve *A B C D E F G*, Fig. 2.)  
Curve of Melting-points.

Percentage of CaO.....	40.0	45.0	48.2	50.0	52	54	55.5	65	67.5
Component in excess melts..	1453°	1500°	1512° <sup>1</sup>	1508°	1484°	1433°	1503°	2080° <sup>2</sup>	2015° <sup>2</sup>

The eutectic *KL* (pseudo-wollastonite +  $\alpha$ -calcium orthosilicate), Table III, was found in all compositions containing more than 50 per cent. and less than 65 per cent. of lime. No trace of it could be detected in the 65 per cent. composition, though diligent search was made for it. A great many determinations were made of it of which only the mean values are given in Table III.

TABLE III.  
(Line *KL*, Fig. 2.)

Eutectic.	Pseudo-wollastonite + $\alpha$ -Calcium Orthosilicate.							
Percentage of CaO...	50	52	54	55.5	57	60	62.5	
Eutectic melts .....	1432°	1430°	1433°	1429°	1431°	1426°	1429°	

The properties of the metasilicate separating along *CD* are also slightly different from those of the pure pseudo-wollastonite, and up to 50 per cent. the mixture appears homogeneous, so that the metasilicate probably takes up about 1 per cent. of orthosilicate in solid solution.

The melting-point of the orthosilicate determined in the iridium furnace was found to be

<sup>1</sup> Determined by Allen and White, Loc. cit.

<sup>2</sup> Determined with the Holborn-Kurlbaum optical pyrometer in the iridium furnace.

$$\begin{array}{r}
 2077^{\circ} \\
 2085^{\circ} \\
 2083^{\circ} \\
 \hline
 \text{Mean, } 2082^{\circ}
 \end{array}$$

Another charge observed at  $2035^{\circ}$  was found to be entirely unmelted. Optical methods of temperature measurement are not competent to determine the melting temperature of the orthosilicate in the presence of the eutectic for reasons already explained (p. 1091), but the eutectic or the compound is readily measured by itself once the composition has been determined. Applying the method to the  $67\frac{1}{2}$  per cent. mixture, therefore, it was found to melt very sharply at  $2015^{\circ}$ . Neither the orthosilicate nor the 70 per cent. lime composition showed any trace of fusion at this temperature. Since the microscopic properties of the orthosilicate remain unchanged in the presence of an excess of lime or of silica, it follows that the orthosilicate does not form solid solutions with either lime or silica. Both eutectics will therefore continue up to the orthosilicate. Above the lime-orthosilicate eutectic the pyrometer affords no further information regarding the melting-point curve.

The line *MN* (Fig. 2) represents the temperature at which the inversion of  $\beta$ -orthosilicate occurs. It will be noted that the inversion is frequently delayed by superheating, especially in the region remote from the eutectic, but it was always possible to show by quenching the material from above and below these temperatures that the variation is merely due to the inevitable lag of the reaction. Between 50 and 65 per cent. of lime, the two heat changes at *MN* and *KL* lie so close together that it was very difficult to separate them. The pyrometer shows two points plainly but each is somewhat displaced by the other. We were able, however, to distinguish them beyond possibility of confusion by holding the furnace constant at  $1425^{\circ}$  and quenching the charge in water. These conditions yield  $\alpha$ -orthosilicate + pseudo-wollastonite, while if the temperature is held at  $1390$ – $1400^{\circ}$ ,  $\beta$ -orthosilicate + pseudo-wollastonite results. The inversion temperatures are contained in Table IV. Mean values are, of course, without significance.

TABLE IV.

		Inversion. $\beta$ -Orthosilicate to $\alpha$ -Orthosilicate.									
Percentage CaO.		55.5	57.0	60.0	62.5	65.0	70	73	75	80	90
Inversion temp.		1407°	1395°	1404°	1396°	1426°	1409°	1426°	1415°	1407°	1438°
		1414	1412	1411	1397	1421	1405	1425	1421	1429	1432
		1403	1419	1411	1405	1415	1412			1432	1433
		1411	1415	1398	1398	1414				1425	
			1406	1402	1408	1412					
			1406	1404	1407	1413					
			1404	1405	1401	1417					
				1388		1423					
						1411					

The scattered points lying below 1300° (Fig. 2) occur only in the compositions in which the metasilicate is present, and correspond, as a microscopic examination at once shows, to the change from wollastonite to the pseudo-hexagonal form. With falling temperature, the points occur very much lower or are lost, since the inversion does not occur quite as readily on cooling. Allen and White observed that this inversion could be brought about only with great difficulty with the pure metasilicate, but in the presence of an excess of either lime or silica, we found it to occur with comparative readiness (Table V) in many compositions. The line *QR* is the temperature at which the reaction  $\beta$  into  $\alpha$  takes place. As observed in the discussion of the properties of the orthosilicate, this reaction does not occur promptly, but is liable to very serious superheating or undercooling.

TABLE V.

		Inversion. $\beta$ -Metasilicate to $\alpha$ -Metasilicate.					
Percentage CaO.		30	32.5	35	40	45	57
Temperature of inversion..		1273°	1274°	1257°	1288°	1254°	1286°
			1263	1399	1266		
				1323			
				1328			

## SUMMARY.

There are only two definite compounds of lime and silica capable of existing in contact with the melt. These two compounds are:

(1) The pseudo-hexagonal metasilicate melting at 1512° and inverting into wollastonite at about 1200°. The metasilicate is able to take up a small amount of either lime or silica in solid solution.

(2) The orthosilicate of calcium which melts at 2080° possesses three polymorphic forms:

The  $\alpha$ -form, which crystallizes in the monoclinic system, has a density of 3.27 and a hardness of between 5 and 6.

The  $\beta$ -modification crystallizes in the orthorhombic system and has a density of 3.28.

The  $\gamma$ -modification has a density of 2.97, and also crystallizes in the monoclinic system. The disintegration or "dusting" of the orthosilicate and of all lime mixtures above 51 per cent. lime is due to the 10 per cent. volume change accompanying the  $\beta \rightleftharpoons \alpha$  inversion.

The inversion point  $\alpha$  to  $\beta$  occurs at  $1410^\circ$ ,  $\beta$  to  $\gamma$  at  $675^\circ$ .

There are three eutectics in the series: Tridymite + the metasilicate at 37 per cent. lime,  $1417^\circ$ ; the metasilicate + orthosilicate at 54 per cent. of lime,  $1430^\circ$ ; and orthosilicate + lime at  $67\frac{1}{2}$  per cent. of lime,  $2015^\circ$ .

The orthosilicate is readily attacked by water, which dissolves out the lime in large quantities. This is probably the reason why it is not found as a natural mineral.

The density of fused lime is 3.32; its hardness 3+. It fuses in the electric arc but its fusion temperature is not accurately measurable. Lime crystallizes in the isometric system and possesses no polymorphic forms.

Silica begins to melt at about  $1600^\circ$  to an extremely viscous liquid, so that an exact melting-point cannot be determined. It has been shown that for all temperatures above  $1000^\circ$  pure quartz changes into tridymite, and pure quartz glass crystallizes as tridymite; so that above this temperature tridymite is unquestionably the stable phase. In the presence of fused chlorides quartz glass crystallizes as quartz at temperatures up to  $760^\circ$  and as tridymite above  $800^\circ$ , crystalline quartz inverts to tridymite above  $800^\circ$  and tridymite goes back to quartz at  $750^\circ$ . The inversion temperature is therefore about  $800^\circ$ , and the change is enantiotropic. The density of pure tridymite was found to be 2.318, and that of quartz glass 2.213. The pure natural quartz used had a density of 2.654, the artificial crystals of 2.650.

Neither the salt of the trisilicic acid,  $2\text{CaO}, 3\text{SiO}_2$ , the *åkermanite* analogue,  $4\text{CaO}, 3\text{SiO}_2$ , nor the tricalcium silicate,  $3\text{CaO}, \text{SiO}_2$ , can exist in the two-component system.

## PLATINUM SILVER ALLOYS.

BY JOHN F. THOMPSON AND EDMUND H. MILLER.

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THE solubility of platinum, when alloyed with silver in nitric acid, may be considered one of the historical facts in the history of the metal, as its announcement by the Graf von Sickingen<sup>1</sup> in 1782, came only forty-six years after the discovery of the element platinum, thus placing it among the earliest known chemical properties. The reasons for and quantitative relations of this solubility have, however, remained unexplained up to the present day, in spite of the numerous attempts on the part of various experimenters. The results of these authors have been conflicting in the extreme, and not only have the later investigators failed to confirm the earlier, but their results in themselves offer no explanation as to the cause of the anomalies. Thus, Clemens Winkler,<sup>2</sup> working with alloys containing percentages of platinum varying from 1 per cent. to 10 per cent., found that the strength of acid used was of small importance, while the weight of residue left, assumed by him to be platinum, was on the average about 66 per cent. of the weight of the original alloy. This percentage varied somewhat irregularly with the strength of acid and percentage of platinum in the alloy, and, in general, decreased with the platinum content of the alloy. John Spiller,<sup>3</sup> on the other hand, investigating alloys of the same range of platinum content, found acid of 1.42 specific gravity to be the best solvent, but records that, even under the most favorable conditions, only 0.75 to 1.25 per cent. of the platinum could be dissolved along with the silver. H. Rose<sup>4</sup> found that, at the most, 10 per cent. went into solution with the silver. N. W. Perry,<sup>5</sup> in a description of an assay method, states that after removing the base metal by cupellation, the platinum could be dissolved completely along with the silver, provided the platinum were alloyed with at least

<sup>1</sup> Muspratt, 4th Ed., 7, p. 255.

<sup>2</sup> Z. anal. Chem. 1874, p. 368.

<sup>3</sup> Pr. Chem. Soc. 13, 118 (1897).

<sup>4</sup> Rose: Handb. Analyt. Chem., 6th Ed., 2, 226.

<sup>5</sup> Eng. Min. J. January, 1879.

twelve times its weight of silver. E. H. Miller,<sup>1</sup> in a comparison of the various wet and assay methods for the determination of platinum, repeated Perry's work and found that, even with a platinum-silver ratio of twenty-seven to one, some platinum remained undissolved. The results in this case were, however, complicated by the presence of iridium and gold in the material experimented on. Later, von den Ropp,<sup>2</sup> in a series of experiments on alloys containing up to 30 per cent. of platinum, found that alloys containing not more than 23 per cent. of platinum could be brought completely into solution by treating them with nitric acid, washing the residue free from nitric acid with water and then treating with hydrochloric acid. Besides this new and positive fact brought out by von den Ropp's work, he also investigated to some extent the black residue left on treating the alloy with nitric acid, and tried the solvent effects of hydrochloric acid, sulphurous acid and ammonia in the order named, the treatment with each reagent being followed with a complete washing of the residue with water, the solutions and wash-waters being kept separate. In this way von den Ropp obtained a series of solutions or colloidal solutions. The cause of the solution of parts of the residue in this way, or the composition of the parts dissolved were, however, not investigated. Finally Krug,<sup>3</sup> in an investigation of the alloys of platinum and copper, found that the residue left on dissolving the alloys in nitric acid, and which he, as well as Winkler and von den Ropp, found to be explosive when heated with organic materials, *i. e.*, filter-paper, consisted of a nitrate. Krug explains the solubility found by von den Ropp (see above), as being merely a reaction of the hydrochloric acid used against this compound giving chlorine which dissolved the platinum. He also advanced the idea that the solutions obtained by von den Ropp with various reagents were simply forms of colloidal platinum. This latter idea will be discussed later in connection with some further solubility experiments. Beside these investigations of the solubilities of the binary alloys of platinum, several papers have been published dealing with experiments on the parting of ternary and even quaternary alloys containing platinum and silver. The results

<sup>1</sup> School of Mines Quarterly, 17, 26 (1895).

<sup>2</sup> Berlin Dissertation, 1900.

<sup>3</sup> Leipzig Dissertation, 1903.

have in most cases been unsatisfactory, as the problem which, in the case of binary alloys, presented wide inconsistencies in similar work done by different investigators, has in the case of ternary and quaternary alloys become so complicated that it is impossible to decide what variable is responsible for any given set of results. The papers dealing with this phase of the subject will, therefore, not be reviewed in full, but will only be referred to when their results have some direct connection with either our experimental results or conclusions. In a foot-note, reference will be found to some of the more important or recent articles.<sup>1</sup>

As may be seen from the foregoing review, neither the primary fact of why platinum dissolves when alloyed with silver, or the secondary facts as to the quantitative relations of this solution have ever been firmly established. Chemical investigation alone would be enough to settle the latter. It is difficult to see, however, how strictly chemical methods could ever solve the first problem or give the basis on which the results of solution tests could be satisfactorily interpreted. The following investigation was therefore started with the idea of studying the physical properties of the platinum silver alloys and using the results so obtained in the interpretation of a series of solubility tests run in comparison with those of previous investigators.

The physical properties chosen for investigation were the melting-points and cooling curves, microstructure, specific gravity and electrical conductivity of the different alloys. These, it was felt, would give a sufficiently wide range of properties, so that reliance could be placed on a confirmation of the results of one series by those of another. A careful survey of the literature was made before beginning this study, with very little result. In this connection the assistance obtained from the excellent bibliographies of Howe<sup>2</sup> and Sack<sup>3</sup> should be acknowledged. On cooling curves the only quantitative data which could be found were given by a partial curve published by Heycock and Neville.<sup>4</sup> These

<sup>1</sup> Carmichael: *J. Chem. Ind.* **22**, 1324 (1903); Sharwood: *Ibid.* **23**, 412 (1904); Richards: *Analyst*, **27**, 265 (1902); Neveu: *Ann. Chim. anal. appl.* **8**, 161; Hollard and Burtiaux: *Ibid.* **9**, 287.

<sup>2</sup> *Bibliography of the Metals of the Platinum Group*. Smithsonian Misc. Collections, Vol. 38, No. 1084.

<sup>3</sup> *Bibliographie der Metallegierung*, *Z. anorg. Chem.* **35**, 249 (1903).

<sup>4</sup> *Phil. Trans.* **189**, A. 25 (1897).



authors investigated alloys containing up to 2 atomic per cent.<sup>1</sup> of platinum (3.55 per cent. by weight) and found that the freezing-point curve rose sharply away from the freezing-point of silver, the alloy containing 2 atomic per cent. of platinum freezing at 990°. Matthiesen,<sup>2</sup> in an account of some experiments on certain platinum silver alloys, refers to the 33 per cent. alloy being at a critical point in electrical resistance. Beyond these references all data that could be found were either inapplicable to the present work or too vague as to percentages of platinum, etc., to be of any use.

#### EXPERIMENTAL.

The first step was the purification of the materials used and the preparation of alloys of known composition and proved homogeneity, the last two points being questions which had been neglected by previous investigators.

*Purification of Materials.*—The platinum used was a supposedly chemically pure foil from a foreign maker, but was shown by qualitative analysis, using the method of Mylius and Dietz,<sup>3</sup> to contain iridium. It was, therefore, freed from this by the following purification method.<sup>4</sup> This consisted in dissolving the impure platinum in aqua regia and freeing from nitric acid by repeated evaporations with hydrochloric acid. This hydrochloric acid solution, containing both of the elements in their highest state of oxidation, was then taken to dryness and heated on an electric hot plate for several hours at a temperature of 125°. It was then taken up with hydrochloric acid and water and precipitated by the addition of ammonium chloride and alcohol. The iridium, which had been reduced by the heating to a lower chloride, not being precipitated by the ammonium chloride, passed into the filtrate along with some of the platinum, also reduced. The

<sup>1</sup> Atomic per cent. may be calculated as follows, for any series of binary alloys A—B:

$$\text{Atomic \% A} = 100 \frac{\frac{\text{weight A}}{\text{atomic weight A}}}{\frac{\text{weight A}}{\text{atomic weight A}} + \frac{\text{weight B}}{\text{atomic weight B}}}$$

Weight A and B  
being taken as  
parts in 100.

Grube: Z. anorg. Chem. 44, 122 (1905).

<sup>2</sup> J. Chem. Soc. 20, 201 (1867).

<sup>3</sup> Ber. 1898, 3137.

<sup>4</sup> Encyclopædia Brit. 9th Ed., 19, 201.

ammonium chlorplatinate was then dried and tested for purity by spreading it out on a glazed paper and examining portions selected from different parts thoroughly under a microscope (80 diameters). In no case, although eight separate portions were examined from each lot, could any salt be detected except the yellow crystals of ammonium chlorplatinate. This salt was then converted to metallic platinum by ignition and washed successively with hydrochloric acid, water, nitric acid and water. The sponge so obtained was either used as such or melted with the oxyhydrogen blowpipe and rolled out into foil.

The silver was guaranteed by a reliable maker to be at least 999 fine, and was used without further purification. As will be shown later, the thermal analysis enabled us to make a check on the purity of the silver by means of a determination of its melting-point.

*Preparation of Alloys.*—To be used for a preliminary survey of the field, five alloys, weighing 10 grams each, were made, containing approximately 10, 20, 30, 40 and 50 per cent. of platinum. The method of preparation was the same throughout, except that the 40 and 50 per cent. alloys were made from the platinum sponge on account of the greater ease of alloying compared with the foil from which the others were made. In all cases, the silver was first melted in a No. 1 French clay crucible in a small Fletcher furnace. After it was thoroughly melted, the platinum was added piece by piece, if used as foil, or wrapped in an ashless filter-paper, when the sponge was employed. Heating was continued for about five minutes, when the crucible was withdrawn from the furnace and shaken violently until the melt solidified. It was then replaced, and this treatment, melting, holding melted for two to three minutes and then removing and shaking until the button solidified, repeated several times. The crucible was then removed from the furnace and the button allowed to solidify and removed from the crucible. It was then replaced in the crucible in an inverted position and the previous treatment repeated, so that any pieces of platinum which might have sunk to the bottom of the button and so escaped the effect of the several shakings, would come more intimately in contact with the melt. After several such heatings the button was allowed to cool and was cut in half vertically. One of the faces so exposed was then polished and examined with a metallographic microscope for any

pieces of unalloyed platinum. If any such were found, the alloy was remelted and the previous treatment repeated until no platinum could be found unalloyed on careful microscopic examination. In cutting the alloys for microscopic examination, considerable difference in their hardness was noted, which will be discussed later in connection with their other physical properties. Before starting the preparation of the alloys, it was feared that the furnace used would not give sufficient heat to melt the alloys of higher platinum content. This fear was, however, without foundation, for using a false top, so that a higher rate of combustion could be used, and also a supplementary blast-lamp of the Waller type, blowing in at the same tuyere hole as the regular blast, it was found that temperatures of  $1450^{\circ}$  could be reached in the crucible.

*Thermal Analysis.*—The freezing-points and cooling curves of the alloys were next taken in the Fletcher furnace, the No. 1 French clay crucible holding the alloy being surrounded by a larger crucible to decrease the rate of cooling. The method used was that of direct observation, using a Siemens and Halske galvanometer and a platinum-platinum 10 per cent. iridium thermocouple. The wires for this couple were made with great care in order to insure perfect homogeneity. In fact the platinum iridium was melted and shotted in water four times before the final ingot was cast. The wires were next thoroughly annealed by means of electrical "glowing" to remove any strains from the wire-drawing and were then investigated and found to be thermoelectrically homogeneous. This was done by taking each wire and connecting one end to each of the terminals of the galvanometer by means of two copper wires, the ends of the platinum or platinum alloy wire being contained in an ordinary cold junction bottle. By heating successive places on the wire, it could be shown that the wire itself was homogeneous throughout, or at least that there were no sudden variations in composition. That the wires were not of progressively changing composition was shown by making each end of the wire successively the hot junction and comparing with a second couple. The maximum error found in this way amounted to  $2^{\circ}$ . This precaution of testing for thermoelectric homogeneity is essential in case it is not desired to make use of more than one junction in a series of determinations of a single point and especially in a Fletcher furnace, where

the length of couple heated can not be easily varied to suit the convenience of the operator. The wires of the couple having been annealed and shown to be homogeneous, the couple was next standardized against the boiling-point of pure sulphur, using a Barus boiling-point tube, and against the freezing-point of Kahlbaum's copper. The sulphur used was in the form of crystals from carbon disulphide and was boiled thoroughly to free from any carbon disulphide, either of crystallization or mechanically held. Its boiling-point was taken at  $444^{\circ}$ .<sup>1</sup> The freezing-point of the copper was taken as  $1084^{\circ}$ <sup>2</sup> and the determinations were made under a layer of charcoal, the copper being melted under this layer, held melted for some time and also poled with a stick to insure complete reduction. From these points the curve of the couple was calculated, using Holman's logarithmic formula.<sup>3</sup> As a check on the accuracy of this curve, the melting-point of Kahlbaum's antimony was next determined, and in all cases fell within a limit of error of  $3^{\circ}$  from the temperature of  $630^{\circ}$  which was taken as the true melting-point.<sup>4</sup> A further check on the accuracy of the standardizing was obtained by the determination of the freezing-point of silver, which was determined in a graphite crucible under a layer of charcoal. This also in every case fell within the  $3^{\circ}$  limit and formed a very good check on the purity of the silver used in the preparation of the alloys. The melting-point of pure silver free from oxygen was taken as  $961^{\circ}$ .<sup>5</sup> In taking the melting-points and cooling curves of the alloys themselves it was not possible to use a charcoal cover, as the disturbing influence of oxygen was preferable to any risk of the platinum forming a carbide or taking carbon into solution. It is probable that this influence was of importance only in the alloys of lower platinum content, as with the higher alloys no noticeable spirting took place. Several experimental difficulties arose in these freezing-point and cooling-curve determinations, due largely to the use of such small amounts of alloys as to make the evolution of heat at any one temperature very small. In all

<sup>1</sup> LeChatelier and Boudouard's "High Temperature Measurements," 2nd Eng. Ed., 296.

<sup>2</sup> Holborn and Day: *Am. J. Sci.* 11, 145 (1901); 8, 165 (1899).

<sup>3</sup> Holman: *Pr. Am. Acad.* 31, 234.

<sup>4</sup> Day and Allen: *Phys. Rev.*, Sept., 1904.

<sup>5</sup> Holborn and Day: *Am. J. Sci.* 11, 145 (1901); 8, 165 (1899).

cases the couple cover was clamped in place so that the end of the couple would come as near as possible to the center of the melt.

*Electrical Resistance, Specific Gravity and Ductility.*—After the thermal analysis had been finished, the alloys were remelted in crucibles of such a shape that the resulting buttons were in the form of cylinders of approximately 9 mm. diameter. A section was cut from the bottom of each button and reserved for microscopic examination while the remainder of the button was rolled out into tape. The rolling out of the alloys was kindly done for me by Mr. Cohn of the platinum-refining firm of Belais & Cohn, of New York City. From this tape a piece of uniform cross-section was cut out, which was thoroughly annealed and used for the measurement of the electrical resistance. This measurement was done for me on a Wolff bridge, by Mr. A. H. Nelson, of the Department of Physics, to whom I wish to express my thanks.

ELECTRICAL RESISTANCE EXPRESSED IN OHMS PER SQUARE MILLIMETER  
PER METER.

0.0	per cent.	platinum	}	0.0217
100.0	"	silver		
10.39	"	platinum		0.0918
20.59	"	"		0.1814
31.46	"	"		0.2914
37.89	"	"		0.3110
57.05	"	"		not determined

The alloys were then cut into small pieces for further investigation by means of a large pair of shears. In this connection the very interesting qualitative fact may be noticed of the very marked change in ductility and in actual hardness which accompanied the increasing platinum content. This had already been noticed when cutting up the alloys for the different microscopic examinations and the same observations were repeated when the alloys were rolled. Thus the pure silver could be cut and rolled in the manner to be expected from its well-known soft and ductile nature; that is, the hack saw was not appreciably dulled by cutting a button and, in rolling, several passes could be made each time before the button had to be annealed. The 10 and 20 per cent. buttons were very much like it in both of these properties. With the increase of the platinum content up to 30 per cent., however, a marked change was noted in the behavior of the buttons. In cutting, the buttons were much harder and this hardness in-

creased rapidly with the increasing platinum content. Thus, while the 31 per cent. button cut with more difficulty than the lower ones, but was still comparatively soft, the 57 per cent. alloy was, on the other hand, so hard that several saws were broken each time a button had to be cut. This property was still more marked in the case of the rolling, and was shown by the increasing frequency with which the alloys had to be annealed in order to get them to go through the rolls without cracking. The limit of this was reached with the 57 per cent. alloy, which would stand almost no reduction and cracked so badly on the first pass that further rolling and, therefore, the measurement of its electrical resistance, had to be abandoned. Since the object of the investigation was to study simply those properties which would tend to throw some light on the chemical behavior, the question of changes in hardness was followed no further and no attempt was made to check these very rough qualitative results by means of sclerometer measurements.

The alloys having been cut up into small pieces, their specific gravity was measured, using a weighing-bottle, as compared to that of water at 4°, with the following results:

Pure silver .....	10.61
10.39 per cent. platinum .....	11.17
20.59 " " " .....	11.80
31.46 " " " .....	12.57
37.89 " " " .....	13.19
57.05 " " " .....	14.25

*Analysis.*—In order that the results on the various alloys might be referred to alloys of known composition, the alloys were analyzed by means of the standard parting with sulphuric acid. From the table of results, given below, the necessity of this step is plainly shown and gives some explanation as to the cause of the anomalous results of some previous investigators, who in no case had any further knowledge of the composition of their alloys than that gained from the proportions used in making them up. As in making our alloys the quantities of the metals were weighed exactly for making alloys of 10, 20, 30, 40 and 50 per cent. of platinum, the magnitude of the error even when working carefully in crucibles may be observed, and shows that the composition of the alloys made on charcoal before a blowpipe can only be a matter of conjecture, no matter how carefully the materials

may have been weighed. As carried out, the parting differed somewhat in detail from that generally described. In fact the methods as given in most descriptions of the process could not fail to give inaccurate results. One description provides for parting 300 mg. of the alloy for fifteen minutes over a Bunsen burner in a parting flask with 10 cc. of pure concentrated sulphuric acid. The acid was then allowed to cool and decanted into a beaker containing distilled water. The residue was treated as before with 5 cc. of strong sulphuric acid, decanted into the same beaker, and washed till free from acid, adding the washings to the silver sulphate solution. The platinum is then transferred to a small crucible by inverting, dried in an air-bath and weighed. By this means the author, working on an alloy containing over 33 per cent. of platinum, obtained results differing only by 0.1 per cent. on four separate determinations, and states that the platinum was tested for silver, but was found to contain only a minute trace. He further states that the silver may be estimated in the filtrate by the thiocyanate method, or, as in his work, by difference.

In attempting to follow out this method it was found that, even with closely agreeing duplicates, entirely erroneous results were obtained, for the following reasons: (1) In decanting the sulphuric acid solution from the residue platinum passed over with the solution. This platinum was in either a very finely divided or colloidal state, giving a dark color to the solution. The state of division was so fine, that not even by allowing the beaker containing the decanted filtrate to stand on a piece of white paper could any particles be seen as such. That they were present, however, is shown by the fact of their separating, if the solution was allowed to stand over night. And further, the fact that this separation on standing was due to particles already contained in the solution, and not to colloidal platinum or to a precipitate formed by some unnoticed reaction during standing, was shown by taking two portions of the same alloy and parting in the same way with sulphuric acid. One of these solutions was decanted and allowed to stand over night, and in the morning a fine black precipitate was found on the bottom of the containing beaker. The second solution was diluted and filtered, when a black precipitate was found on the filter-paper, and the filtrate on standing threw down no further precipitate. (2) The platinum

residue left, always contained some silver. This was less in amount with the lower platinum alloys, but was always a weighable quantity, and in the higher alloys became of very considerable importance. The use of the thiocyanate method for determining the silver in the filtrate was tried, but was not successful, in the presence of the large amounts of sulphuric acid from the solution of the alloy. By precipitating the silver from this acid solution with aluminium foil, dissolving in nitric acid and titrating, better results could be obtained, but the duplicates were not satisfactory.

The method finally adopted was as follows: 300 mg. of the alloy were taken and heated for fifteen minutes in a beaker with 10 cc. of concentrated sulphuric acid on an asbestos pad over a Bunsen burner. This solution was then decanted into a beaker and the alloy broken up by poking the pieces with a stirring rod, and then re-treated for fifteen minutes with 5 cc. more of concentrated sulphuric acid. The solutions were then combined, diluted, filtered through an ashless paper, and washed till entirely free from silver salts. The residue on the paper was then ignited in a porcelain crucible and weighed. This residue was then dissolved in aqua regia and by several treatments with nitric acid, followed by taking the solution gently down almost to dryness most of the free acid was removed, and the free acid that remained was nitric and not hydrochloric. The solution was then diluted somewhat, and the silver precipitated by the addition of common salt in the usual way. The precipitate obtained in this manner was of a reddish yellow color, apparently due to admixed silver chlorplatinate. This precipitate was filtered and washed free from chlorides. It was then dissolved through the paper with dilute ammonia and reprecipitated in the filtrate with nitric acid and a drop or two of hydrochloric acid. It was filtered and weighed in the regular way. It was found that this solution of the impure silver chloride and reprecipitation gave a perfectly white precipitate, while the platinum passed into the filtrate. The strong sulphuric acid solution containing the silver was treated in one of two ways: (1) By diluting to about 900 cc., partly neutralizing and precipitating the silver as sulphide at a temperature of about  $90^{\circ}$ , filtering, dissolving the sulphide in nitric acid and reprecipitating the silver as chloride, in which form it was weighed. (2) The effect of precipitating the silver as chloride direct in the sulphuric acid solution with common salt, after partly neutralizing with



ammonia, was tried with practically the same results as obtained by the first and longer method of procedure. In either case the precipitated silver chloride was washed till the washings gave no test with silver nitrate, while the filtrates were all tested with hydrogen sulphide to be sure that the summations obtained were not due to any balancing of errors. The sulphuric acid used in the parting was tested and found to contain no nitric acid. In some cases, however, unweighable traces of platinum could be found in the filtrate, by means of an examination with a microscope on the concentrated filtrate when tested with ammonium chloride. This was neglected in our work, and no attempt was made to separate it from the silver, which it contaminated, as the amount present was very small.<sup>1</sup> The results follow:

Pt supposed.....	10.00	20.00	30.00	40.00	50.00
Pt actual.....	10.39	20.59	31.46	37.89 <sup>2</sup>	57.05
Ag retained by Pt.....	tr.	0.59	0.98	2.24	2.70
Ag in filtrate.....	89.54	78.62	67.51	59.81	40.26
Summation .....	99.93	99.80	99.95	99.94	100.01

As may be seen from the previous tables, these results have been used to correct the supposed platinum percentages on the alloys.

*Microstructure.*—The specimens which had been reserved for the microscopic examination were next prepared for examination and photographing by polishing them successively on rough and smooth Armour emery paper, and on 0, 00, 000 and 0000 Hubert French emery paper. The polishing was finally finished on baize on a rouge board, using carefully washed jewelers' rouge. Etching was done with 1.1 specific gravity nitric acid. For examining and photographing the alloys, a Reichert microscope was used in connection with a Bausch and Lomb photomicrographic

<sup>1</sup> Recently in a paper published by Delépine (Compt. rend. 142, 631 (1906); abs. J. Chem. Ind. 25, 314 (1906)), it has been claimed that boiling concentrated sulphuric acid will dissolve considerable amounts of platinum on treatment for forty to fifty hours. This is in direct contradiction to other work on the same lines (Conroy: J. Chem. Ind. 22, 465 (1903)) but whether true or not has no application to our experiments where the time of treatment was much less.

<sup>2</sup> The very low platinum content of this alloy can only be explained by the accidental loss of platinum during the preparation, as duplicates show that the figure for platinum as given above is correct, and repeated microscopic examinations of polished sections show that it is homogeneous.

camera, using a Welsbach illumination and an inside illuminator. All photographs were taken at a magnification of 100 diameters.

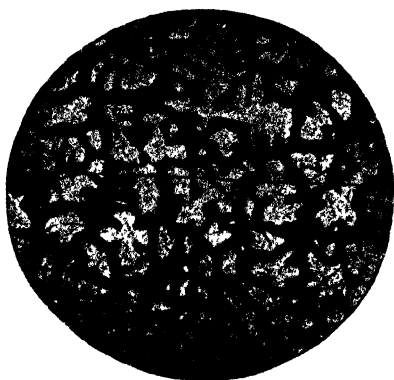
*Results of Thermal Analysis and Microscopic Examination.*—Heycock and Neville,<sup>1</sup> in their investigation of a limited portion of the platinum silver cooling curve, found that with increasing platinum content, up to the limit of their investigation, the melting-point rose regularly, their alloy of maximum platinum content (3.55 per cent.) having a melting-point of 990°. In our experiments the alloy containing 10.39 per cent. of platinum was heated to 1200°, and the cooling curve taken from that point. Two evolutions of heat were noticed, the first at 1045–1050° and the second and much larger at 1000°. Owing to the conditions of radiation from the furnace there was always a slight drop of temperature throughout, when operating with weights of alloys as small as 10 grams, and it was not possible to determine whether solidification was complete at 1000° or not. The alloy, when examined under the microscope, was found to consist of crystals set in a ground mass, which was not composite, or at least, which could not be resolved by the highest power available. This is not, however, a positive proof that the ground mass had not frozen out as a eutectic and afterward become simple by segregation, a fact of common occurrence when the eutectic is small in amount. The 20.59 per cent. alloy was heated to 1100°, and on cooling evolved heat strongly at 1085°, and possibly again at 995°, although the indications at the latter point were hardly beyond the experimental error. The microstructure at this point showed large, white dendrites also set in a non-composite ground mass. The 31.46 per cent. alloy was heated to 1300° and a cooling curve taken down to 970°. Marked evolutions of heat took place in the range between 1170° and 1100°. They were, however, very irregular and were different in their exact location in different trials. The examination of the alloys under the microscope showed well-defined crystals of a grayish color set in a dark ground mass. These gray crystals had each a perfectly white silvery core or spine, which offers a clue to the irregularities of the cooling curves. This is, that the rate of cooling was so rapid that the alloy passing through transformation points did not have time to come to equilibrium, and this result is shown both by the microstructure and by the cooling curves. In the cooling curves this is shown

<sup>1</sup> Loc. cit.

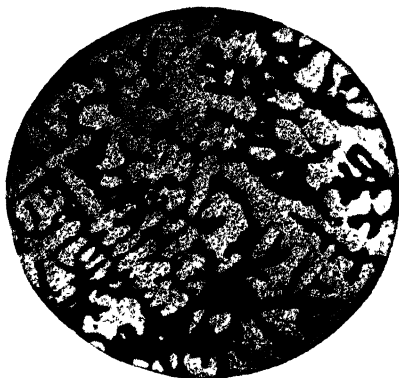
by the heat liberations at any one temperature being very small and also confused, owing to heat liberations from two separate causes taking place at the same time in different parts of the button. The most regular of the curves show, however, a consistent evolution of heat at  $1160^{\circ}$ , and this is taken as probably correct. There are also weak indications at about  $1230^{\circ}$ . In the microphotographs this is shown by the white core in the centre of the crystals, which disappears when the alloy is remelted and allowed to solidify and cool very slowly in a gas furnace (see photomicrographs). The 37.89 per cent. platinum alloy, while showing much the same characteristics in its microstructure as the 31.46 per cent. alloy, *i. e.*, gray crystals with white centres set in a dark ground mass, gives much sharper heat evolutions during its cooling. These are at  $1240^{\circ}$ , not very strong but consistent for all curves, and a second at  $1170^{\circ}$ , which is strongly marked in all curves, and is the most marked evolution for this particular alloy. Unfortunately, the curve was only once continued below  $1000^{\circ}$ , and in this case was too irregular to be of any value. The 57.05 per cent. alloy was heated to over  $1400^{\circ}$ , and on cooling gave evolutions of heat at  $1240^{\circ}$ ,  $1180^{\circ}$  and  $1090^{\circ}$ . In microstructure it appeared very much like the 37 per cent. alloy.

#### SOLUBILITY TESTS IN NITRIC ACID.

*Method of Procedure.*—Chemically pure nitric acid was diluted with distilled water and, after cooling, the concentration was adjusted with water to 1.1 specific gravity to within the limit of accuracy of a delicate hydrometer. Three hundred mg. of each of the alloys, cut into small pieces ( $1 \times 2 \times 2$  mm.) were next weighed out into No. 2 beakers and 25 cc. of the 1.1 acid added to each. These were placed on an electric hot plate and heated rapidly to  $70^{\circ}$  or  $80^{\circ}$  and kept at that temperature for an hour, the temperature being observed by means of thermometers. At the end of twenty minutes the alloys were broken up by means of the thermometers, so as to prevent as far as possible the effect of any mechanical coating. After an hour the solutions were removed from the stove and allowed to stand for one and one-quarter hours after diluting to about 75 cc. The solutions were all somewhat colored, those from the 20 and 31 per cent. alloys especially, the order of decreasing intensity of color being 20, 31, 37, 57 and 10. Of these the 20 was almost black and was



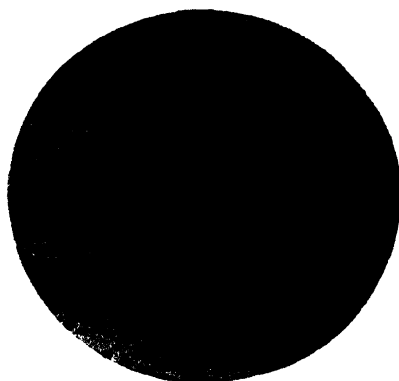
10.39 per cent. platinum  
Air-cooled.



20.59 per cent. platinum.  
Air-cooled.



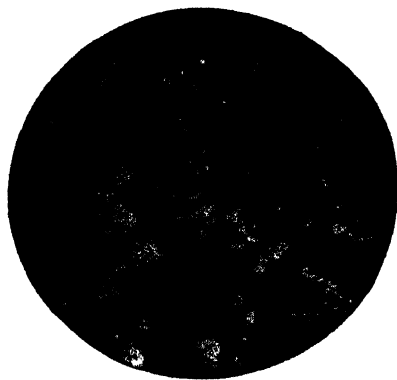
31.46 per cent. platinum.  
Air-cooled



31.46 per cent. platinum.  
Furnace-cooled.



37.89 per cent. platinum.  
Air cooled.



57.05 per cent. platinum.  
Air-cooled.



opaque, the remainder rapidly shaded down in color to the 10, which was almost colorless. The solutions were then filtered through 7 cm. ashless filter-papers, when it was found that the filtrates bore the same color relation as the original solutions. On attempting to wash the precipitates with distilled water, they washed through the paper readily and acted in the manner common to all colloidal precipitates. The filtrates and wash solutions were therefore combined and the residues salted out with sodium nitrate free from chloride. After standing they were filtered through the same filter-paper as before, and on washing with 1 per cent. nitric acid (*i. e.*, 1 cc. of 1.42 acid in 100 of water) it was found that they could be washed free from silver without loss from the formation of any colloidal precipitate. After ignition in porcelain crucibles they were weighed, dissolved in aqua regia and the silver contained determined as in the case of the analysis of the alloys. During the ignition, slight explosions due to the precipitate reacting with the filter-paper could always be noticed. The results follow, the one given for the 31.46 per cent. alloy being determined on the alloy in the rapidly cooled state.

Per cent. Pt in alloy.....	10.39	20.59	31.46	37.89	57.05
" " residue.....	3.86	8.58	36.59	49.13	65.16
" " Ag in residue.....	0.27	1.81	12.09	13.64	12.19
" " Pt in residue.....	3.59	6.77	24.50	35.49	52.97

Evidently, from the foregoing any ratio of platinum and silver which will allow of complete solution of both in nitric acid of 1.1 specific gravity must lie within considerably closer ranges than those investigated above. A further series of alloys was therefore made in order to test further for this point. These alloys were made in the same way as the previous set and were examined microscopically for homogeneity. Parting tests were conducted as before with nitric acid of 1.1 specific gravity, except that the silver content of the residues was not determined, as the object was to find a completely soluble ratio, or failing that the most nearly soluble ratio to test the process as a means for analytical separation. Since Miller's<sup>1</sup> work had shown that with a platinum content of 4 per cent. some residue was left, the alloys below that point were investigated thoroughly. Besides these, alloys were

<sup>1</sup> Loc. cit.

made at ratios selected by means of the cooling curves and certain alloys were selected arbitrarily in order that the solubility results might not have to be interpolated except over very narrow ranges. The results follow, those for the 31.46 per cent. alloy in this case being on the very slowly cooled alloy.

Per cent. Pt in alloy....	0.50	1.00	2.00	3.00	4.00	5.00	
" " residue.....	0.42	0.85	1.74	2.19	2.98	3.56	
" " Pt in alloy....	13.00	14.00	15.00	16.00	18.00	25.00	31.46
" " residue.....	3.33 <sup>1</sup>	4.26	4.32	4.55 <sup>1</sup>	4.54 <sup>1</sup>	16.62	38.58

In these tests as well as those of the previous series the formation of colloidal platinum was very marked, especially with the alloys near to 20 per cent. of platinum. When this had been completely removed by means of ammonium nitrate and heat, the solutions were still colored, but this coloration was very slight and no further separation took place in solutions containing considerable ammonium nitrate and nitric acid, even on standing several days.

As previous investigators had found that the amount of residue varied with the strength of acid used, a further series was run, using nitric acid of 1.40 specific gravity as a solvent. The method of procedure was the same as that of the previous series, the results being as follows:

Per cent. Pt in alloy	0.50	1.00	2.00	3.00	4.00	5.00	10.00	
" " residue.....	0.22	0.42	1.09	1.81	2.42	2.62	4.53	
" " Pt in alloy	13.00	14.00	15.00	16.00	18.00	20.00	25.00	30.00
" " residue.....	5.79	4.97	7.93	11.54	11.65	13.94	20.66	29.29

The foregoing results show clearly the impossibility of separating platinum from gold, iridium, etc., when alloyed with silver by means of one parting with nitric acid, and also the fallacy of assay methods, such as Perry's, based on this supposed separation. The questions as to the explanation of the solubilities are, however, more complex. From the results of etching tests made on the stage of the microscope it is apparent that the reaction of the alloy with the nitric acid is a double one, part tending to give solution of the alloy and part tending to produce the explosive nitro compound, well-known as one of the products of this reaction. This in itself would explain many of the differences shown by the work of various investigators working on alloys of

<sup>1</sup> Average of two figures.

the same composition. A second cause enters in, however, which is probably the more important. It is as follows: From the thermal data and microstructure it may be seen that the alloys consist of a series of solid solutions, having several reaction or transformation temperatures where the crystals already separated out react with the molten part of the alloy. On account of the high melting-point of these alloys, the cooling through these ranges is always so rapid that these reactions are never complete and the final alloy consists of a variety of products upon whose individual solubilities depend the solubility of the alloy as a whole.

Attempts were made to isolate the different components of the alloys by means of solution with various reagents. These were, however, all futile, as it was not possible to find in the time at our disposal, any reagent which would give a complete solution of one constituent without attack on the remainder of the alloy. In the course of this work the 37.89 and 57.05 per cent. platinum alloys were remelted and quenched in cold water from the molten state, and polished slips were submitted to the action of nitric acid of 1.2 specific gravity in the cold for a period of about ten days, the object being to isolate the constituent first to freeze out. The acid was changed frequently and the products of the reaction were removed by washing by decantation with cold water. The slips of alloy, even after being so disintegrated that they felt apart on being pressed with a stirring rod, retained their bright appearance, showing that one constituent at least was apparently unattacked by the acid. In no case was it possible, however, to carry the treatment so far that standing in fresh acid for twenty-four hours gave no attack, as shown by the presence of silver in the solution. Whether this was due to some attack on the apparently insoluble constituent or to the continued solution of undissolved ground mass could not be determined. The residues were finally washed thoroughly and examined under a microscope when they were found to consist of grains which were apparently unattacked. Analysis of these grains while, sufficiently concordant to point to a definite platinum silver compound, did not justify the assignment of a formula. Coupled with the marked and increasing hardness and brittleness of the alloys containing more than 30 per cent. of platinum, which properties are lacking in both of the metals forming the alloys and persist



even in the annealed samples, we are led to conclude that a platinum silver compound crystallizes out which reacts against the liquid during solidification, giving a soluble or partially soluble product, which in turn further reacts or is transformed. The explanation of the abnormal solubilities of these alloys and of the widely differing results of the different investigators therefore lies in the presence of varying amounts of these constituents, depending both upon the composition and rate of cooling of the alloy.

#### CONCLUSIONS.

(1) The separation of platinum from gold, iridium, etc., in one operation by means of alloying with silver and parting with nitric acid is impossible.

(2) Analytical results on platinum silver alloys, based on parting with concentrated sulphuric acid, are incorrect for alloys containing 20 per cent. or more of platinum, unless correction is made for the undissolved silver remaining with the platinum.

(3) The existence of platinum silver compounds is probably the explanation of the irregular results obtained in parting with nitric acid.

QUANTITATIVE LABORATORY, COLUMBIA UNIVERSITY,  
June 27, 1906.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 128.]

### THE INSOLUBLE CHROMICYANIDES.<sup>1</sup>

BY FREDERICK VAN DYKE CRUSER AND EDMUND H. MILLER.

Received June 7, 1906.

As the potassium salt of hydrochromicyanic acid was used to precipitate the others, the methods of preparing the salts were first considered.

In 1903 L. O. Beatty investigated the method of preparation of potassium chromicyanide, and found that the methods of Böckmann,<sup>2</sup> Stridsberg,<sup>3</sup> Kaiser<sup>4</sup> and Christensen<sup>5</sup> did not give

<sup>1</sup> Read at the May Meeting of the New York Section of the American Chemical Society.

<sup>2</sup> *Traité de Chimique Organique*, J. Liebig, Vol. I, p. 174; Gmelin's "Handbook of Chemistry," Vol. VII, p. 420; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; *Jahresb.* 1864, Vol. XVII, p. 302.

<sup>3</sup> *Jahresb.* 1864, Vol. XVII, p. 304; *N. Arch. ph. nat.* XXII, p. 151.

<sup>4</sup> *Ann. Chem. Pharm.* III suppl., p. 163; Gmelin *Handb.* 4

satisfactory results. The method finally adopted by him was a modification of the method of Christensen, which is as follows:

The chromium chloride and potassium chloride obtained by reduction of 50 grams of potassium dichromate with alcohol and hydrochloric acid, after evaporation, were dissolved in 150 cc. of water. This solution was heated, and added slowly to a hot solution of 100 grams of potassium cyanide dissolved in 200 cc. of water, stirring constantly. The mixture was digested hot for several hours. This was filtered, and evaporated *in vacuo* to concentration, filtered from the separated chromium hydroxide, and cooled in an ice mixture. The crystals were filtered off, and washed first with dilute (50 per cent.), and then with strong alcohol (95 per cent.). No alcohol was used for precipitating the salt. The salt was recrystallized as often as necessary to free it from potassium chloride. Contrary to what Kaiser states, Beatty says that the potassium chromicyanide is decomposed by boiling even in a vacuum.

His yield was less than 50 per cent.

#### EXPERIMENTAL.

In carrying out this work, we are indebted to Mr. L. O. Beatty, who furnished some of the potassium chromicyanide. This salt was purified by recrystallizations over sulphuric acid in a vacuum.

Some potassium chromicyanide was prepared by Beatty's method, but the method finally used, after also testing Christensen's method, was a modification of the former. Sixty grams of chromium trioxide were dissolved in 150 cc. of concentrated hydrochloric acid, and 75 cc. of water. Seventy-five cc. of 95 per cent. alcohol were added to the mixture, a little at a time, and then the solution was evaporated to dryness. The residue was dissolved in 225 cc. of boiling water, and added slowly to a hot solution of 150 grams of potassium cyanide dissolved in 300 cc. of water. The solution was stirred vigorously after each addition of the chromium solution. The mixture was digested for several hours, and then filtered on a Büchner funnel. The filtrate was allowed to evaporate in the air, large yellow crystals

auf. 4, 335; Gmelin's "Handbook of Chemistry," VII, p. 429; "Handwörterbuch d. Chem. Fehling," p. 663; Jahresb. 1864, Vol. XVII, p. 302; Chem. Centrbl., 1865, p. 259.

<sup>6</sup> J. pr. Chem. 139, 2, 31, 163 (1885); [2] 23, 52. .

of potassium chromicyanide forming, which were very pure, and consequently required only one or two recrystallizations.

If a large excess of potassium cyanide is used, a thick, deep red solution is obtained, from which alcohol will not precipitate potassium chromicyanide, but a syrup is formed at the bottom of the dish.

The salt heated five hours at  $100^{\circ}$  in a water-jacketed air-bath did not lose in weight. When heated at  $102^{\circ}$  in an air-bath for three hours, there was no loss in weight.

Three grams heated to  $147^{\circ}$  lost 0.7 mg. At this temperature the salt has a deep reddish yellow color.

At  $159^{\circ}$  the salt began to decompose, losing 2.3 mg. in weight, the crystals turning dark in spots. The temperature was increased, and at  $196^{\circ}$  the total loss in weight was only 3.2 mg. On ignition at a red heat the substance becomes black, and melts, the residue finally having a green color ( $\text{Cr}_2\text{O}_3$ ). The crystals decrepitate when strongly heated.

One gram of pure potassium chromicyanide was dissolved in 300 cc. of water, and the solution allowed to stand in the light for several weeks at the ordinary temperature. The salt slowly decomposed, the solution becoming cloudy.

One gram of the salt heated red hot in a porcelain boat in a glass tube gave no water of crystallization.

0.7026 gram of the salt was analyzed by the following method: It was decomposed by boiling with aqua regia, the solution being boiled down with concentrated hydrochloric acid several times to get rid of the excess of nitric acid. The solution was finally diluted with water, and the chromium precipitated three times from the boiling hot solution by ammonium hydroxide in slightest excess. The filtrates were evaporated to dryness, and ignited to drive off the ammonium salts, the residue taken up with water, evaporated again, and ignited. The weight of the impure potassium chloride gave 36.3 per cent. of potassium.

The residue was dissolved in hot water, an excess of chlorplatinic acid added, and the solution evaporated. More chlorplatinic acid was added, then alcohol, until about 75 per cent. by volume, and the solution allowed to stand over night in a platinum dish. The potassium chlorplatinite was filtered, washed, dissolved by boiling water into a weighed platinum dish,

and after evaporation, weighed. Weighing the potassium as sulphate did not give satisfactory results.

The precipitate of chromium hydroxide was washed into a porcelain casserole, and treated with an excess of sodium peroxide. The solution was boiled for fifteen to twenty minutes, after the addition of more peroxide.

The solution was allowed to cool, and then diluted with water to 500 cc. volume. This was made acid by 10 cc. of concentrated sulphuric acid in excess, and titrated by a standard solution of ferrous sulphate (64.052 grams per liter), using a spot test, with a very dilute, freshly prepared solution of potassium ferricyanide. The ferrous sulphate was standardized at the same time by titration against a weighed quantity of potassium chromate, using the above conditions. This was the method used for the determination of chromium throughout the work.

Before this method was decided upon, 0.5207 gram of potassium chromate was dissolved in water, the chromium reduced in a hydrochloric acid solution by alcohol, and precipitated as chromium hydroxide. This was treated as above (sodium peroxide, etc.), and required the same number of cubic centimeters of ferrous sulphate solution as the same weight of potassium chromate, both solutions being titrated under the same conditions.

The addition of an excess of Mohr's salt to the acid chromate solution, and subsequent titration with a standard potassium permanganate solution, did not give accurate results, as the end point was obscured by the green chromium salt formed. When the precipitated chromium hydroxide was ignited and the chromium weighed as sesquioxide, the results were slightly high, due to the occlusion of salts by the hydroxide, sulphates especially causing this trouble.

The nitrogen was determined by the Kjeldahl method, using 0.5005 gram for analysis.

		Calculated. Per cent.	Found. Per cent.
3K .....	117.45	36.05	36.01
Cr.....	52.1	15.99	16.03
6C.....	72.0	22.1	by difference 21.97
6N .....	84.24	25.86	25.99
		<hr/> 100.00	<hr/> 100.00

The formula  $K_3Cr(CN)_6$  is therefore confirmed.

The following reagents were used for determining the chemical properties of the chromicyanides.

Concentrated hydrochloric acid, sp. gr. 1.20; concentrated nitric acid, sp. gr. 1.42; concentrated sulphuric acid, sp. gr. 1.84; dilute hydrochloric acid, sp. gr. 1.0815; dilute nitric acid, sp. gr. 1.232; dilute sulphuric acid, sp. gr. 1.186; acetic acid, sp. gr. 1.017; ammonium hydroxide (strong), sp. gr. 0.900; ammonium hydroxide (dilute), sp. gr. 0.9775.

Double normal sodium hydroxide; double normal sodium carbonate; normal potassium cyanide; aqua regia (1 part concentrated nitric + 3 parts concentrated hydrochloric acid); sodium peroxide; ammonium sulphide.

Potassium chromicyanide is decomposed by boiling with water and sodium peroxide. The solution, made acid with acetic acid, gives a yellow precipitate with lead acetate.

It is decomposed by concentrated hydrochloric acid, in the cold, more readily on boiling, giving a green solution.

It is decomposed by concentrated nitric acid, giving a green solution on boiling.

It dissolves slowly in concentrated sulphuric acid, giving a yellow solution, which, on boiling, decomposes, giving a red, violet, and then a green solution.

It is decomposed by dilute sulphuric, hydrochloric or nitric acids, giving a green solution readily on boiling.

Aqua regia decomposes the salt more readily on heating.

*Cadmium Chromicyanide*,  $\text{Cd}_3\text{Cr}_2(\text{CN})_{12}$ .—According to Kaiser<sup>1</sup> cadmium salts give a white precipitate. We prepared the salt, first, by adding a 4 per cent. solution of cadmium chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of cadmium chloride. In both cases, a white precipitate with a slightly greenish tinge immediately formed. This was washed thoroughly by decantation and dried at 100°.

The compound decomposed readily on ignition in a porcelain crucible, giving cadmium oxide and metallic cadmium which deposited on the cover of the crucible. Consequently, this method could not be used for decomposing the compound for analysis.

For analysis about 0.4 gram of the substance was decomposed by dissolving in dilute hydrochloric acid and evaporating twice

<sup>1</sup> Ann, III Suppl., p. 170.

to a small bulk to secure complete decomposition. The cadmium was then precipitated as sulphide, the latter dissolved in dilute hydrochloric acid, and after evaporation, neutralization and the addition of 1 gram of potassium cyanide, the solution was electrolyzed by 0.17 ampere and 3.75 volts. The chromium was determined as already described.

The analyses gave: Cd, 41.45, 41.72; Cr, 12.76, 12.93. Calculated for  $\text{Cd}_3\text{Cr}_2(\text{CN})_{12}$ : Cd, 44.73; Cr, 13.82. Ratio of Cr to Cd: I, 2:3.01; II, 2:2.99.

The formula given to the compound, therefore, is  $\text{Cd}_3\text{Cr}_2(\text{CN})_{12}$ .

Cadmium chromicyanide is readily soluble in an excess of potassium cyanide, and ammonium hydroxide.

Concentrated hydrochloric acid immediately decomposes it, giving a red solution, which becomes green. This takes place more quickly on boiling. Concentrated nitric acid has the same effect, but the action is slower in the cold. Concentrated sulphuric acid acts more slowly than either of the above.

Dilute hydrochloric, nitric and sulphuric acids decompose the compound, giving off hydrocyanic acid, and forming green solutions quickly on boiling, but slowly in the cold. Aqua regia dissolves it quickly. On boiling with sodium peroxide, it is decomposed.

The compound is decomposed by ammonium sulphide, sodium hydroxide and sodium carbonate.

Acetic acid decomposes the compound slowly on boiling.

*Cobalt Chromicyanide*,  $\text{Co}_3\text{Cr}_2(\text{CN})_{12}$ .—Berzelius<sup>1</sup> states that cobalt salts give a brown precipitate, which remains brown when dry. As given in Watts' Dictionary,<sup>2</sup> chromicyanide of cobalt is a blue precipitate. According to Gmelin,<sup>3</sup> salts of protoxide of cobalt yield a blue precipitate with sesquicyanide of chromium. Kaiser<sup>4</sup> states that cobalt salts give with potassium chromicyanide a flesh-colored precipitate insoluble in acids, but soluble in ammonium hydroxide, giving a yellow solution. The salt was prepared, first, by adding a 4 per cent. solution of cobalt nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a

<sup>1</sup> Berzelius Lehrbuch, 1845, Vol. III, p. 1075.

<sup>2</sup> Watt's Dict. Chem., Vol. II, 1872, p. 205.

<sup>3</sup> Gmelin's "Handbook of Chemistry," Vol. VII, p. 495.

<sup>4</sup> Ann. III Suppl., p. 170; ["Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb., 1864, p. 302.

4 per cent. solution of cobalt nitrate. In both cases a light rose-colored precipitate was formed. These were washed thoroughly by decantation, magnesium chloride being added from time to time when the precipitate became colloidal, and dried at  $100^{\circ}$ . The color of the dried sample was yellowish brown.

For analysis, 0.3 to 0.5 gram was ignited in a porcelain crucible, and fused with sodium peroxide. The fusion was leached out with water, and the precipitate filtered, washed and dissolved in dilute sulphuric acid. After neutralization, 100 cc. of ammonium hydroxide and 3 grams of ammonium sulphate were added, and the solution electrolyzed by 2.5 amperes and 4.75 volts. The chromium was determined as before.

The analyses gave: Co, 22.86, 21.64; Cr, 13.59, 12.65. Calculated for  $\text{Co}_3\text{Cr}_2(\text{CN})_{12}$ : Co, 29.81; Cr, 17.55. Ratio of Cr to Co: I, 2:97; II, 2:3.02.

The formula  $\text{Co}_3\text{Cr}_2(\text{CN})_{12}$  is therefore given to the compound when precipitated either by an excess of the cobalt salt or the potassium chromicyanide.

Cobalt chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by boiling with sodium peroxide, giving a black precipitate, and a yellow solution of chromate. It is also decomposed by ammonium sulphide. Ammonium hydroxide decomposes the compound, but does not entirely dissolve it. Sodium hydroxide decomposes the compound rapidly, sodium carbonate slowly. It is insoluble in cold or boiling acetic acid. Concentrated sulphuric acid, and concentrated hydrochloric acid dissolve it in the cold, very readily on boiling. It is not readily soluble in concentrated nitric acid, even on boiling.

Aqua regia decomposes the compound, but it is not entirely dissolved, even on boiling. It is very slowly soluble in dilute sulphuric, hydrochloric, or nitric acids, being least soluble in the last. On boiling, dilute sulphuric and hydrochloric acids readily dissolve it, but nitric acid, only slowly.

*Cuprous Chromicyanide*,  $\text{Cu}_3\text{Cr}(\text{CN})_6$ .—Kaiser<sup>1</sup> states that by treating cupric chromicyanide with a stream of hydrogen sulphide, or by sulphurous acid, a red compound is formed, which is probably cuprous chromicyanide ( $3\text{Cu}_2\text{Cy.Cr}_2\text{Cy}_8$ , equivalent to  $\text{Cu}_3\text{Cr}(\text{CN})_6$  at present).

One gram of potassium chromicyanide was treated with a

<sup>1</sup> Ann. III Suppl., p. 166.

slight excess of a solution of cuprous chloride, in about 75 cc. bulk. An orange-yellow precipitate immediately formed, which was filtered, washed thoroughly, and dried at  $100^{\circ}$ . For analysis, about 0.5 gram was dissolved in dilute nitric acid, evaporated to low bulk, water added, and a little ammonium hydroxide, and the solution electrolyzed, using a current of 0.35 ampere and 2.1 volts.

Some chromium was oxidized by the current to chromate. Consequently, after all the copper was deposited, the electrolyte was boiled with alcohol, and then the chromium precipitated as chromium hydroxide, and determined as before.

The analysis gave: Cu, 45.01; Cr, 12.24. Calculated for  $\text{Cu}_3\text{Cr}(\text{CN})_6$ : Cu, 47.80; Cr, 13.05. Ratio of Cr to Cu, 1:3.01. The formula of the compound is therefore  $\text{Cu}_3\text{Cr}(\text{CN})_6$ .

Cuprous chromicyanide is readily soluble in an excess of potassium cyanide and readily dissolved by concentrated nitric acid in the cold or on boiling. Dilute nitric acid dissolves it, very quickly on boiling. It is readily decomposed by aqua regia, giving a green solution. It is decomposed by concentrated hydrochloric acid, slowly going into solution in the cold, but quickly on boiling. The dilute acid acts similarly.

Cold concentrated sulphuric acid dissolves it slowly, but quickly on boiling. The dilute acid acts similarly, but more slowly than with the concentrated acid. On boiling with the dilute acid it dissolves quickly, giving a green solution.

*Cupric Chromicyanide*,  $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$ .—Kaiser<sup>1</sup> states that in the cold, copper sulphate gives a blue precipitate, containing a little potassium, as shown by his analysis, and which he calculates to copper. By mixing at  $75^{\circ}$  a concentrated solution of a copper salt with dilute potassium chromicyanide solution, the precipitate was free from potassium.

From his analysis he gives the formula  $3\text{CuCy}.\text{Cr}_2\text{Cy}_3$ , corresponding to  $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$  at the present time.

On heating this compound formed in the cold, at  $40^{\circ}$ , it loses water irregularly, and if the temperature is raised, it changes from blue to blue-green, green, yellow-green, and finally reddish-gray at  $100^{\circ}$ , carrying variable amounts of water. This red salt, on being treated with water, will not become blue again. It is

<sup>1</sup> Ann. III Suppl., p. 166; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).



insoluble in cold acids, dilute or concentrated, but dissolves on heating. Also insoluble in cold ammonium hydroxide, and sodium hydroxide. On boiling with the latter, dark brown copper oxide is finally precipitated.

Comey<sup>1</sup> gives the formula  $\text{Cu}_3(\text{Cr}(\text{CN})_6)_2$  to the cupric compound, and states that it is a precipitate insoluble in dilute or concentrated acids, except on heating; insoluble in ammonium or potassium hydroxides plus water.

We prepared the salt, first, by adding a 3 per cent. solution of copper sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 3 per cent. solution of potassium chromicyanide to a 2 per cent. solution of copper sulphate. In both cases, a precipitate immediately formed, having a robin's egg-blue color, which changed to green on standing. Both precipitates were thoroughly washed by decantation, potassium sulphate and magnesium chloride being used with the latter as it became very colloidal, and dried at  $100^\circ$ . The color of the dried substance was reddish purple.

For analysis, about 0.5 gram was dissolved in dilute nitric acid, and after boiling for about two hours, the solution was electrolyzed. The chromium was precipitated as hydroxide, and determined as usual.

The analyses gave: Cu, 32.23, 30.96; Cr, 17.50, 16.96. Calculated for  $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$ : Cu, 31.41; Cr, 17.15. Ratio of Cr to Cu: I, 2:3.02; II, 2:2.99.

The formula  $\text{Cu}_3\text{Cr}_2(\text{CN})_{12}$  is therefore given to this compound, being precipitated either by an excess of the copper salt, or *vice versa*.

Cupric chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by an excess of ammonium hydroxide in the cold, giving a blue solution, and a precipitate. Ammonium sulphide gives a black precipitate of copper sulphide. It is decomposed by sodium hydroxide, and by sodium carbonate, the latter giving a blue solution, and a yellowish green precipitate.

It is dissolved by aqua regia; readily by concentrated sulphuric acid in the cold, giving a red solution, which becomes violet, and finally green. Concentrated hydrochloric acid readily dissolves it in the cold, more quickly on boiling. Concentrated nitric acid decomposes it, but only gives a clear green solution on boiling. It

<sup>1</sup> "Dictionary of Solubilities," 1896.

is very slowly soluble in cold dilute hydrochloric, nitric, and sulphuric acids, while on boiling the first two readily dissolve it, but the sulphuric acid dissolves it only slowly. It is insoluble in cold acetic acid.

Boiled with sodium peroxide and water, it is decomposed, giving a green solution. On the addition of acetic acid, a precipitate formed. This was removed by filtration and then lead acetate added to the filtrate, and a yellow precipitate of lead chromate obtained.

*Ferrous Chromicyanide*,  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$ .—According to Kaiser,<sup>1</sup> potassium chromicyanide gives with ferrous solutions, a red, very pulverulent precipitate. If precipitated at  $70^\circ$  it is practically potassium-free, two analyses averaging 0.25 per cent. of potassium. If heated to  $100^\circ$  there is a great loss of hydrocyanic acid, and the black mass resulting no longer dissolves by warming with hydrochloric acid, while the compound dried over sulphuric acid readily dissolves in hydrochloric acid. To the substance dried over sulphuric acid he gives the formula  $3\text{FeCN}.\text{Cr}_2(\text{CN})_3.20\text{Aq.}$ , corresponding to  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}.20\text{Aq.}$  at the present time, but states that the point at which the compound has not yet lost any water is very difficult to determine accurately, because the substance contains so much water of crystallization. The substance is decomposed by shaking with sodium hydroxide. Liebig<sup>2</sup> states that potassium chromicyanide gives a brick-red precipitate with ferrous salts. Watts<sup>3</sup> states that the precipitate is brick-red, while Storer<sup>4</sup> gives the formula  $3\text{FeCN}.\text{Cr}_2(\text{CN})_3$  (?), equivalent to  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$  at present.

We prepared the salt, first, by adding a 7 per cent. solution of Mohr's salt to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of Mohr's salt. In both cases, two drops of concentrated sulphuric acid were added. A brick-red granular precipitate formed immediately in each case, which was washed thoroughly by decantation, and dried at  $100^\circ$ . The color of the dried substance was dark green.

<sup>1</sup> Ann. III Suppl., p. 169; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

<sup>2</sup> "Traité de Chimique Organique," J. Liebig, Vol. I, p. 174.

<sup>3</sup> Watt's "Dictionary of Chemistry," 2, 205 (1872).

<sup>4</sup> Storer: "Dictionary of Solubilities," 1864.

For analysis, from 0.3 to 0.5 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, dissolved in sulphuric acid, and the iron determined by titration with permanganate. The chromium was determined as before.

The analyses gave: Fe, 22.12, 22.06; Cr, 13.85, 13.75. Calculated for  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$ : Fe, 28.70; Cr, 17.83. Ratio of Cr to Fe: I, 2:2.98; II, 2:2.99. Therefore, the formula of the compound is  $\text{Fe}_3\text{Cr}_2(\text{CN})_{12}$ .

Ferrous chromicyanide is decomposed by sodium hydroxide and ammonium hydroxide, giving a brown precipitate, by sodium carbonate giving a green precipitate, and by ammonium sulphide. Potassium cyanide immediately turns the precipitate dark-red, but does not dissolve it. It is decomposed by boiling with sodium peroxide and water.

Aqua regia immediately decomposes the compound, in the cold or on boiling. It is most soluble in hydrochloric acid, concentrated or dilute acid slowly dissolving it in the cold, but very quickly on boiling, giving a green solution.

Dilute or concentrated nitric acid, in the cold, decomposes it, giving a precipitate of a dirty yellow color. On boiling with the dilute acid, a clear solution is obtained, but the precipitate does not dissolve on boiling with the concentrated acid, except when diluted with water. Concentrated sulphuric acid immediately decomposes it, hot or cold. Cold dilute sulphuric acid acts more slowly than hydrochloric acid but, on boiling, a clear solution is quickly obtained. It is not decomposed by cold acetic acid.

*Manganous Chromicyanide*,  $\text{Mn}_3\text{Cr}_2(\text{CN})_{12}$ .—Kaiser<sup>1</sup> states that the manganese salt is white, crystalline, and insoluble in dilute acids.

We prepared the salt, first, by adding a  $3\frac{1}{2}$  per cent. solution of manganese chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of manganese chloride. In both cases, a greenish white precipitate immediately formed, which, under the microscope, appeared to consist of small crystals, apparently isometric. The precipitates were washed thoroughly, and dried at  $100^\circ$ ; when dried, the color was light brown.

<sup>1</sup> Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

If the compound is dried in a desiccator, in a vacuum, over sulphuric acid, it has a buff color.

The compound was analyzed by several methods. A portion was ignited in a porcelain crucible, and then fused with sodium peroxide, but this introduced silica and alumina, which had to be subsequently separated, and the results were very poor. Another portion was dissolved in hydrochloric acid, and the chromium precipitated four times by ammonium hydroxide. The manganese could not be separated from the chromium by this method. The filtrates were combined, the manganese separated, and potassium determined, giving only a trace.

Finally, about 0.5 gram of the compound was dissolved in dilute hydrochloric acid, and after two evaporations to low bulk with acid, sodium peroxide was added, and the solution boiled. The precipitate was filtered, washed, and dissolved in dilute hydrochloric acid and sulphurous acid. The sulphur dioxide was boiled out of the solution, and the preceding process repeated four times until the manganese was free from chromium, when it was determined as manganese pyrophosphate. The chromium was determined as before.

The analyses gave: Mn, 23.06, 23.14; Cr, 14.58, 14.69. Calculated for  $\text{Mn}_3\text{Cr}_2(\text{CN})_{12}$ : Mn, 28.37; Cr, 17.91. Ratio of Cr to Mn, I, 2 : 2.99; II, 2 : 2.98.

The compound has, therefore, the formula  $\text{Mn}_3\text{Cr}_2(\text{CN})_{12}$ .

The compound is decomposed by sodium peroxide, giving a precipitate of manganese dioxide, and a yellow solution of chromate; decomposed by boiling with concentrated hydrochloric, nitric or sulphuric acid or aqua regia, giving a green solution; readily soluble in an excess of potassium cyanide; decomposed by an excess of ammonium hydroxide, sodium hydroxide, sodium carbonate and ammonium sulphide; dissolves very slowly in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a green solution; only slightly soluble in cold acetic acid, more so on boiling.

*Mercurous Compound.*—According to Berzelius,<sup>1</sup> mercurous salts give a white precipitate with potassium chromicyanide, which makes the solution at the bottom brown, while the precipitate becomes dark. The color of the liquid soon disappears,

<sup>1</sup> Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

and a compound of chromium cyanide with a little mercury remains behind.

Kaiser<sup>1</sup> states that mercurous nitrate gives a dark gray precipitate with potassium chromicyanide, insoluble in nitric acid and ammonium hydroxide.

We dissolved 0.5 gram of potassium chromicyanide in 50 cc. of water, and quickly added 100 cc. of a 2 per cent. solution of mercurous nitrate.

A yellowish white precipitate formed, which quickly darkened, turning finally to gray, and which settled rapidly. The solution did not then smell of hydrocyanic acid. One hundred cc. of water were added, and the solution stirred. The precipitate settled rapidly, leaving the supernatant liquid reddish-yellow, which rapidly became darker in color. The precipitate darkened, becoming smaller in volume, and on stirring the solution hydrocyanic acid could be readily detected. On standing for a day or so the solution became green, due to the color of the chromium salt. The gray precipitate proved to be nothing but metallic mercury in a very finely divided state. This was filtered and washed, dissolved in dilute nitric acid, part of the acid neutralized by ammonium hydroxide and the solution electrolyzed by a current of 0.18 ampere, and 2.3 volts.

Total weight of mercury found was 0.4679 gram.

The reaction takes place probably in the following steps: First, mercurous chromicyanide is precipitated, which then decomposes, giving mercurous cyanide, which then decomposes, giving mercuric cyanide, which slowly dissolves, and metallic mercury.

If the reaction takes place as above stated, 0.5 gram of the potassium salt would precipitate 0.4605 gram of mercury, while 0.4679 gram was found.

*Nickel Chromicyanide*,  $\text{Ni}_3\text{Cr}_2(\text{CN})_{12}$ .—Kaiser<sup>1</sup> states that solutions of nickel salts give a bluish-green precipitate, very voluminous, becoming green on boiling, insoluble in dilute acids, but soluble in ammonium hydroxide with a grayish green color.

The salt was prepared, first, by adding a 4 per cent. solution of nickel nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of nickel nitrate. In both

<sup>1</sup> Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

cases a voluminous light greenish blue precipitate formed immediately which was washed thoroughly by decantation, with the aid of 8 grams of magnesium chloride, added from time to time, when it became too colloidal. The precipitates were dried at  $100^{\circ}$ , when they became black in color.

Five-tenths gram of the substance was dissolved by dilute nitric acid, and the separation of the chromium from the nickel attempted by the addition of ammonium hydroxide, in the presence of ammonium chloride, and reprecipitation of the chromium. The results were inaccurate. Finally 0.3 to 0.6 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, and dissolved in dilute sulphuric acid. After the addition of 3 grams of ammonium sulphate, and 100 cc. of ammonium hydroxide in excess, the solution was electrolyzed by a current of 2.5 amperes and 3 volts. The chromium was determined as before.

The analyses gave: Ni, 24.25, 18.13; Cr, 14.37, 10.76. Calculated for  $\text{Ni}_3\text{Cr}_2(\text{CN})_{12}$ : Ni, 29.71; Cr, 17.58. Ratio of Cr to Ni, I, 2:3.00; II, 2:2.99. Number II was not dry when analyzed.

The formula  $\text{Ni}_3\text{Cr}_2(\text{CN})_{12}$  is, therefore, given to the compound, being precipitated either by an excess of nickel salt or of potassium chromicyanide.

The substance is readily soluble in an excess of potassium cyanide and ammonium hydroxide. It is readily decomposed by ammonium sulphide. It dissolves slowly in the cold in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a clear green solution.

It is slowly soluble in concentrated hydrochloric, nitric, or sulphuric acid, being much more soluble in concentrated sulphuric acid than in either of the other two. On boiling, all three acids readily dissolve it, forming clear green solutions.

It is slowly decomposed by aqua regia in the cold, quite readily on boiling, giving a green solution after a few minutes.

On boiling with sodium peroxide and water, it is decomposed, but not very readily, precipitating green nickel hydroxide. The filtrate contains sodium chromicyanide. Sodium hydroxide behaves similarly. Sodium carbonate decomposes it slowly in the

cold. The compound is insoluble in cold acetic acid, but is slightly soluble on boiling.

*Silver Chromicyanide*,  $\text{Ag}_3\text{Cr}(\text{CN})_{12}$ .—Berzelius<sup>1</sup> states that silver salts give a white precipitate with potassium chromicyanide, which is gray when dry.

Kaiser<sup>2</sup> states that silver chromicyanide is of a deep yellow color, and in the dry state unaffected by light. It is noted for its stability, being unaffected after twelve hours' treatment with hydrochloric acid, nitric acid, or ammonium hydroxide. He says that the only solvent is potassium cyanide, and that hydrochloric acid reprecipitates silver chromicyanide. Dried at  $20^\circ$  to  $30^\circ$ , it retains its yellow color, while at  $100^\circ$  it has a rose-red color, and loses 0.6 per cent. of its weight. He gives the formula  $3\text{AgCN}.\text{Cr}_2\text{CN}_3$ , equivalent to  $\text{Ag}_3\text{Cr}(\text{CN})_6$  at present, and states that there was some undecomposed substance in the silver chloride, making the percentage of silver high and the chromium low. According to Watts,<sup>3</sup> silver nitrate gives a white precipitate.

Stover<sup>4</sup> gives chromicyanide of silver  $3\text{AgCN}.\text{Cr}_2(\text{CN})_3$ , equivalent to  $\text{Ag}_3\text{Cr}(\text{CN})_6$  at present, as a precipitate. Comey<sup>5</sup> says that silver chromicyanide  $\text{Ag}_3\text{Cr}(\text{CN})_6$  is insoluble in all solvents excepting potassium cyanide.

Böckmann<sup>6</sup> states that potassium chromicyanide forms a white precipitate with silver salts similar in composition to the potassium salt. When heated, it decomposes into cyanogen gas, metallic silver and chromium cyanide. Hydrogen sulphide passed through the solution containing silver chromicyanide in suspension, gives silver sulphide, and hydrochromicyanic acid.

We prepared the salt by adding a 4 per cent. solution of silver nitrate to a 2 per cent. solution of potassium chromicyanide. An orange-yellow voluminous precipitate immediately formed, which settled rapidly, and was easily washed by decantation, and dried at  $100^\circ$ ; when dry, it was rose-red in color.

Difficulty was encountered in the analysis of this compound.

<sup>1</sup> Berzelius' "Lehrbuch," Vol. III, 1075-76 (1845).

<sup>2</sup> Ann. III Suppl., p. 167; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

<sup>3</sup> Watts' "Dictionary of Chemistry," 2, 205 (1872).

<sup>4</sup> "Dictionary of Solubilities," 1864.

<sup>5</sup> "Dictionary of Solubilities," 1896.

<sup>6</sup> Gmelin's "Handbook of Chemistry," Vol. VIII, p 31; "Traité de Chimie Organique," J. Liebig, Vol. I, p. 174.

The substance was dissolved in concentrated nitric acid and dilute sulphuric acid, and heated for some time. The silver was precipitated as silver chloride, which gave about 0.7 per cent. of silver too high, and about 0.5 per cent. of chromium too low. This corresponds quite closely to the results given by Kaiser.<sup>1</sup> Several analyses were made with the same result. It was thought that the difficulty was with incomplete decomposition of the silver compound. Consequently, the following method was finally used, giving good results:

About 0.5 gram of the substance was treated with concentrated nitric acid and dilute sulphuric acid, the solution boiled down to low bulk, more nitric acid added, and the treatment repeated three times, finally evaporating until nearly all the nitric acid was eliminated. If the solution is evaporated too far, a sulphate of chromium will be formed, which is then insoluble on the addition of more acid and boiling. The solution was allowed to cool, and then a little dilute hydrochloric acid was added to precipitate the silver. The silver chloride was filtered on a porcelain Gooch crucible, with a piece of filter-paper on the bottom, and dried at  $110^{\circ}$  and weighed. The silver chloride was dissolved in 3.25 grams of potassium cyanide, and the solution electrolyzed.

The chromium was determined as before.

The analyses gave: Ag, from electrolysis, 60.84; from AgCl, 60.89; Cr, 9.69. Calculated for  $\text{Ag}_3\text{Cr}(\text{CN})_6$ : Ag, 60.85; Cr, 9.79. Ratio of Cr to Ag: from electrolysis, 1:3.03; from AgCl, 1:3.04.

The formula  $\text{Ag}_3\text{Cr}(\text{CN})_6$  is confirmed.

Silver chromicyanide is readily soluble in an excess of potassium cyanide, giving a yellow solution. Ammonium sulphide decomposes the compound, precipitating black silver sulphide. It is decomposed by sodium hydroxide solution, and slightly by ammonium hydroxide. It is insoluble in a solution of sodium carbonate, as in hot or cold acetic acid. By boiling with sodium peroxide and water it is decomposed.

A large excess of concentrated hydrochloric acid dissolves the compound, the solution becoming red, then pink, and finally green. On dilution with water, silver chloride is precipitated. When treated with small amounts of acid the decomposition is the same,

<sup>1</sup> Kaiser: Ann. III Suppl., p. 167.



only silver chloride is precipitated. With concentrated nitric acid it slowly dissolves, giving a yellow solution. On boiling it quickly dissolves, giving a green solution.

It is readily soluble in an excess of concentrated sulphuric acid, the solution becoming red, then pink and finally green.

It is decomposed by aqua regia, giving a precipitate of silver chloride. It is very slightly soluble in cold dilute hydrochloric acid, but decomposes on boiling, giving a green solution and a precipitate of silver chloride. It is slightly soluble in cold dilute nitric acid, but even on boiling is not entirely dissolved. Dilute sulphuric acid does not attack it as readily as dilute nitric acid, being only very slightly soluble in the cold, but much more soluble on boiling.

*Zinc Chromicyanide*,  $\text{Zn}_3\text{Cr}_2(\text{CN})_{12}$ .—According to Berzelius<sup>1</sup> zinc salts give a white precipitate with potassium chromicyanide, bluish gray when dry.

Kaiser<sup>2</sup> states that the zinc precipitate is yellowish white in color, pulverulent, and easily soluble in ammonium and sodium hydroxides, but only incompletely decomposed by alkali carbonates. It is insoluble in dilute acids, but somewhat concentrated acids color the compound red, and the solution also.

Gmelin<sup>3</sup> says that the zinc compound is white, turning light bluish gray when dry.

Storer<sup>4</sup> says that chromicyanide of zinc is a precipitate.

Watts<sup>5</sup> states that a solution of potassium chromicyanide gives a white precipitate with zinc salts.

We prepared the salt, first, by adding a 4 per cent. solution of zinc sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of zinc sulphate. In both cases, a yellowish white precipitate immediately formed, which, under the microscope, appeared to consist of very small crystals, apparently isometric. The precipitates were thoroughly washed and dried at 100°. When dried over sulphuric acid, at the ordinary temperature, the compound has a straw color.

<sup>1</sup> Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

<sup>2</sup> Ann. III Suppl., p. 169; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

<sup>3</sup> Gmelin's "Handbook of Chemistry," Vol. VII, p. 425.

<sup>4</sup> Storer's "Dictionary of Solubilities," 1864.

<sup>5</sup> Watts' "Dictionary," Vol. II, p. 205 (1872).

About 0.5 gram of the substance was dissolved in sulphuric acid, and the chromium precipitated four times by ammonium hydroxide, dissolving the precipitate each time in a considerable excess of hydrochloric acid. From the results obtained it was found that the separation of chromium from zinc was not complete.

Another sample was analyzed as before, with the exception that the zinc was precipitated first as sulphide after taking out the chromium as before. The sulphide of zinc was dissolved in hydrochloric acid, and the zinc precipitated as before. The results again showed incomplete separation of chromium and zinc. Finally about 0.5 gram of the substance was dissolved in aqua regia, and the solution boiled down to low bulk several times in a casserole after the addition of hydrochloric acid. The solution was finally diluted with water to a volume of about 400 cc., and neutralized by ammonium hydroxide, and then made fairly acid with acetic acid, and a stream of hydrogen sulphide passed through the solution in the cold for about two hours.

The zinc sulphide was filtered, washed, and dissolved in hydrochloric acid, and the zinc determined as pyrophosphate. The chromium was determined as before. Potassium was determined as chlorplatinate, giving 0.35 per cent. of potassium, which was somewhat impure from a little organic matter from the alcohol.

The analyses gave: Zn, 29.42, 31.01; Cr, 15.68, 16.41. Calculated for  $\text{Zn}_3\text{Cr}_2(\text{CN})_{12}$ : Zn, 32.01; Cr, 17.00. Ratio of Cr to Zn: I, 2:2.99; II, 2:3.01.

The formula of the compound is therefore  $\text{Zn}_3\text{Cr}_2(\text{CN})_{12}$ .

Zinc chromicyanide is readily soluble in an excess of potassium cyanide, sodium hydroxide, and ammonium hydroxide. It is decomposed by sodium carbonate solution. Ammonium sulphide decomposes the compound, precipitating white zinc sulphide. Boiled with sodium peroxide and water it gives a clear yellow solution, which yields a yellow precipitate of lead chromate on the addition of lead acetate and acetic acid.

With concentrated hydrochloric acid it decomposes slowly, but very quickly on boiling, giving a red, then green solution. It is readily decomposed by boiling with concentrated nitric or sulphuric acid, giving a green solution in each case.

Aqua regia decomposes it quickly, giving a clear red solution, which becomes green.

Dilute hydrochloric acid in the cold easily dissolves the compound, yielding finally a green solution. Dilute sulphuric acid acts more slowly, while dilute nitric acid decomposes it very slowly. On boiling, any of the three readily yields a green solution. It is very slightly soluble in boiling acetic acid.

*Lead Compounds.*—Böckmann<sup>1</sup> states that potassium chromicyanide gives a white precipitate with basic lead acetate, but no precipitate with lead nitrate. Berzelius<sup>2</sup> says that lead salts give a white precipitate, which becomes blue on drying. Kaiser<sup>3</sup> states that the neutral lead salt is soluble in water. On evaporation, hydrocyanic acid is given off, the solution becomes green and a grayishwhite pulverulent substance separates. He says that it is easy to obtain a basic lead chromicyanide by adding to the yellow solution containing the neutral salt a mixture of lead acetate and ammonium hydroxide. Also that basic salts can be formed from hydrochromicyanic acid. He thinks that several of these basic salts exist, as on adding to the filtrates either lead acetate or ammonium hydroxide, he obtains repeatedly new compounds containing chromium. Also that the precipitates formed are sometimes easily soluble in an excess of lead solutions, or that the filtrates are precipitated by diluting with water. In other cases this did not happen. He analyzed one of the compounds, and from the results obtained concluded that it was a mixture of different basic salts. The compound was easily soluble in nitric acid and sodium hydroxide solution.

We found that tenth-normal solutions of lead nitrate and lead acetate, with a few drops of acetic acid, gave no precipitate with tenth-normal potassium chromicyanide solution, either when added in excess, or *vice versa*.

*Soluble Chromicyanides.*—Kaiser<sup>3</sup> states that mercuric chloride and stannous chloride solutions behave the same as lead. He states that aluminium, chromium, ferric iron or uranium, gives no precipitation with potassium chromicyanide in the cold, while, on heating, the potassium salt is decomposed. According to

<sup>1</sup> Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

<sup>2</sup> Berzelius' "Lehrbuch," Vol. III, pp. 1075-76 (1845); Gmelin's "Handbook of Chemistry," Vol. VII, p. 428.

<sup>3</sup> Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 303 (1864).

Böckmann<sup>1</sup> the salts of ferric iron give no precipitate; also given by Watts.<sup>2</sup>

We found that tenth-normal solutions of the following reagents gave no precipitate with tenth-normal potassium chromicyanide, either when added in excess, or *vice versa*.

Aluminium sulphate, barium chloride, calcium chloride, bismuth nitrate (with enough nitric acid to prevent hydrolysis), ferric chloride, lithium chloride, magnesium sulphate, mercuric nitrate (with a few drops of nitric acid added to dissolve the salt), mercuric chloride, strontium chloride, sodium chloride, ammonium chloride, caesium chloride, rubidium chloride, chromium chloride, arsenic acid, cerous sulphate, antimony chloride (with enough hydrochloric acid to keep the antimony in solution), antimony chloride, with enough tartaric acid to keep the antimony in solution, erbium nitrate, beryllium nitrate, didymium nitrate, ammonium molybdate, lanthanum nitrate, platinum chloride (chlorplatinic acid), sodium chlorplatinate, sodium tungstate, ammonium vanadate, uranium nitrate, columbium potassium fluoride ( $K_2NbOF_6$ ), tantalum potassium fluoride (a saturated solution only), arsenious acid (a saturated solution only), stannous chloride (with enough hydrochloric acid to keep the salt in solution), thorium nitrate, thallium sulphate, yttrium nitrate, zirconium nitrate (with a few drops of nitric acid to clear the solution).

A 5 per cent. solution of palladium chloride and a solution of auric chloride gave no precipitate when added in excess, or *vice versa*, to a tenth-normal solution of potassium chromicyanide.

From the foregoing results, we see that the insoluble chromicyanides, formed by the ordinary methods of precipitation, are all normal in composition, in this respect as well as regards their solubility, resembling the cobalticyanides more closely than the ferricyanides. The fact of their normal composition, and the intense red color of the ferrous compound, may lead to their use in volumetric analysis, but whether they are insoluble enough to give accurate results further investigation must decide.

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June 4, 1906.

<sup>1</sup> Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

<sup>2</sup> Watts' "Dictionary of Chemistry," Vol. II, p. 205 (1872).

## IRON AND CALCIUM.

By OLIVER P. WATTS.

Received July 13, 1906.

Now that calcium has become available for experimental purposes, and could no doubt be produced cheaply enough for commercial use, provided there were a large demand for it, any new experiments with this metal, although they have yielded results of no constructive value, may yet contribute something to our all too scanty knowledge of the properties and uses of this interesting element. It is with this in mind that an account of the experiments which follow is presented. One of the most promising fields for the use of calcium would seem to be in metallurgy, particularly in the metallurgy of iron, where it might prove an efficient substitute for the deoxidizing agents—silicon, manganese, and aluminum. In addition to its action as a deoxidizing agent, calcium might be expected to be of value in removing sulphur and phosphorus from iron. A proposal to use calcium for these purposes raises the question of the extent to which any excess of calcium will alloy with the iron, and its effects upon the latter metal. These are the questions concerning which some preliminary experiments have been made.

Four attempts were made to form alloys of calcium with iron by fusing together the two metals. In order to prevent oxidation of the calcium before the iron reached its melting-point, the calcium was hammered into a cavity drilled in a cylinder of pure iron, and an iron cap either screwed or hammered tightly into the opening, so that it would have required an internal pressure of several hundred pounds per square inch to force out the cap. The cylinder was placed in a crucible of Acheson graphite lined with magnesia, tightly covered with the same materials, and heated in an electric furnace of the resistance type until the iron melted. Owing to the low density of calcium, the weight of this metal used in each case was small.

	I	II.	III.	IV.
Weight of calcium taken.....	1.6	4.5	6.0	14.3
Per cent. of calcium taken.....	0.23	1.4	0.77	3.78

The results as to the alloying of the two metals were uniform—no calcium was found in the melted iron. Two changes in composition were, however, made by the calcium. In IV the content

both of silicon and of carbon was increased to 0.32 per cent. silicon and 0.218 per cent. carbon. The same iron melted under like conditions, but, without the calcium, contains 0.01 to 0.09 per cent. silicon and 0.03 to 0.04 per cent. carbon, so that the actual increase was 0.83 gram silicon and 0.65 gram carbon. The first thought would naturally be that this increase of silicon and carbon was due to impurities in the calcium used, but this would require that metal to contain 5.8 per cent. silicon and 4.5 per cent. carbon. The gas evolved by the action of this calcium on water had only the faintest odor, and burned with a non-luminous flame, indicating the absence of any considerable amount of calcium carbide. The calcium came from Germany and was not analyzed by the writer, but analysis of similar metal by B. Larsen<sup>1</sup> gave 0.11 per cent.  $\text{CaC}_2$ . The only tenable inference seems to be that the silicon and carbon are reduction products of the action of the calcium upon silica present as impurity in the magnesia lining, and upon carbon monoxide in the atmosphere within the crucible. In previous attempts to produce alloys of iron high in aluminum, by melting together the two metals in a similar crucible buried in a carbon resistor, the reducing action upon the carbon monoxide was so great as to form large amounts of aluminum carbide. It was therefore expected that calcium would act similarly, and it is only surprising that the extent of this action was not greater. In this connection the action of calcium upon carbon dioxide was tested by kindling a thin piece of the metal in the air, which was difficult to do with the highest heat of a Bunsen burner, and plunging it into a jar of the gas. It burned brilliantly, much more so than in air, leaving as solid products, lime, calcium carbide and carbon. A further attempt at alloying iron and calcium was made by heating 2 grams of calcium within a cylinder of pure iron for seventeen hours at  $850-880^\circ$ . The calcium melted, but no trace of alloying was found. C. Quasebart, of Aachen,<sup>2</sup> also obtained negative results in several attempts to alloy calcium with iron.

As a last resort in the endeavor to alloy iron with calcium, iron oxide was reduced by calcium filings in the presence of excess of calcium. The charge, consisting of 42 grams calcium filings, 60 grams pulverized  $\text{Fe}_3\text{O}_4$ , and 20 grams of calcium in lumps,

<sup>1</sup> Chem. Centr. 2, 1466 (1905).

<sup>2</sup> Electrochem. Met. Ind. May, 1906, p. 190.

was put into a magnesia crucible. This was enclosed in a strong steel cylinder, devised by Professor C. F. Burgess for firing thermite and similar charges under great pressure, and kindly placed at the disposal of the author. The charge was fired electrically by means of an iron fuse-wire. The reaction was very vigorous and resulted in a metallic ingot and several small pellets. In cold water gas was slowly evolved from the metal at a few points on the surface and calcium hydroxide was formed. For analysis a small piece was heated for three hours in water until all evolution of gas had ceased. It was then washed, dissolved in hydrochloric acid, and found to contain 0.3 per cent. of calcium. Although this amount of calcium came from the interior of the mass of metal, in view of the failure of all other attempts to make an alloy it seems probable that the calcium was imprisoned by the sudden cooling after reaction occurred and held mechanically, not alloyed with the iron.

The diffusion of phosphide of iron through solid iron at high temperatures has been pointed out by J. O. Arnold.<sup>1</sup> Experiments were tried to see if calcium, when heated in contact with iron containing phosphorus and sulphur, would diminish the amounts of these elements sufficiently for the change to be detected by the microscope. To prepare metal for this treatment, coarsely pulverized electrolytic iron was mixed with sulphur and placed in a magnesia-lined crucible, while red phosphorus was enclosed in a cylinder of pure iron and placed in another crucible; both were melted in the electric furnace.

	For sulphur.	For phosphorus
Weight of iron in charge.. .. .	372.4 grams.	438.62 grams.
Weight of non-metal in charge .. . . .	7.6    "	13.5    "
Percentage of non-metal in charge.....	2	2.76
Percentage of non-metal found.....	0.3	1.96
Weight of non-metal combined with iron	1.13 grams.	8.62 grams.

Holes were drilled in the ingots; into these were put 5.0 grams and 7.3 grams of calcium respectively, and the openings were closed by caps of pure iron. The ingots were packed in powdered magnesia in a crucible, and heated five hours, at 1200-1300° in a gas furnace. They were badly oxidized, particularly at the tops. All calcium had vanished and the ingot had become perfectly homogeneous, except that the boundaries of the cavity which had contained the calcium could still be distinguished.

<sup>1</sup> J. Iron Steel Inst. 1894, I, p. 107.

Each ingot was of the same structure throughout, the caps of pure iron having the same appearance under the microscope as the rest of the ingot. Dark areas, probably of phosphide eutectic, were distributed quite uniformly throughout the ingots. The calcium in this experiment was probably oxidized partially, and perhaps wholly, by oxide of iron.

In the same way calcium was melted with iron containing phosphorus and sulphur. Eight grams of calcium removed all of the 0.37 gram of sulphur present in one ingot, and 11 grams of calcium removed 0.61 gram out of a total of 6.04 grams of phosphorus present in the other ingot, thus reducing the percentage of the latter element from 1.96 to 1.56.

These experiments show:

1. That iron and calcium do not form alloys.
2. That by the reduction of the oxides of carbon the latter element may be introduced into fused metals to which calcium is added.
3. That any commercial application of calcium to the removal of phosphorus from iron is impracticable.

The above observations were made incidental to an investigation of iron alloys, now in progress under a grant from the Carnegie Institution.

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## THE CONSTITUTION OF PARIS GREEN AND ITS HOMOLOGUES.

BY S. AVERY.

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### INTRODUCTION.

COPPER aceto-arsenite, under the names of Paris green, Schweinfurt green, and many others, has been a commercial product for nearly a century. The first contribution to its chemistry that I am able to find was made by Liebig.<sup>1</sup> The first definite statement in regard to its composition was made by Ehrmann,<sup>2</sup> working in Liebig's laboratory, who found it to consist of 3 molecules of copper meta-arsenite crystallized with 1

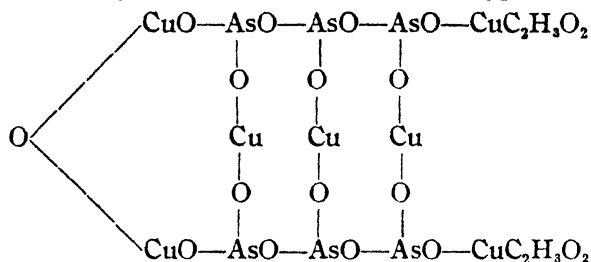
<sup>1</sup> Liebig u. Poggendorf's *Handwörterbuch der reinen und angewandten Chemie*, 1848, 703.

<sup>2</sup> *Ann.* 12, 92.



molecule of copper acetate. Abraham<sup>1</sup> found that formic, butyric or valeric acid could be substituted for acetic acid, but does not seem to have made an analysis of the products. Wöhler<sup>2</sup> found that in a butyric green made by him 2 molecules of copper meta-arsenite are united with one of the copper butyrate.

Speculation in regard to the constitution of Paris green have not been wanting, thus Schiff and Sestini<sup>3</sup> suggest the following:



Such a formula would yield

	Per cent
As <sub>2</sub> O <sub>3</sub> .....	47.40
CuO.....	44.46
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> .....	8.14

whereas the formula of Ehrmann requires

	Per cent
As <sub>2</sub> O <sub>3</sub> .....	58.55
CuO.....	31.39
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> .....	10.06

and numerous analyses of the purest samples do not show a variation of more than 3 per cent. of arsenious acid, 1 per cent. copper and 0.4 per cent. of acetic anhydride from Ehrmann's formula.

In comparatively recent years doubt has been expressed as to whether Paris green of a definite chemical composition can be produced. Six years ago the writer and Beans,<sup>4</sup> as the result of numerous analyses and relying to some extent on the opinions of other chemists, used the expression "Since Paris green is a compound of no very definite composition," etc. Stillman,<sup>5</sup> referring to Ehrmann's formula, says: "This formula is empirical, since a portion of the arsenic may exist as arsenic acid, and copper sub-

<sup>1</sup> Chem. News, 21, 265.

<sup>2</sup> Ann. 94, 44.

<sup>3</sup> Ann. 228, 91.

<sup>4</sup> This Journal, 23, 116.

<sup>5</sup> Chem. News, 80, 250.

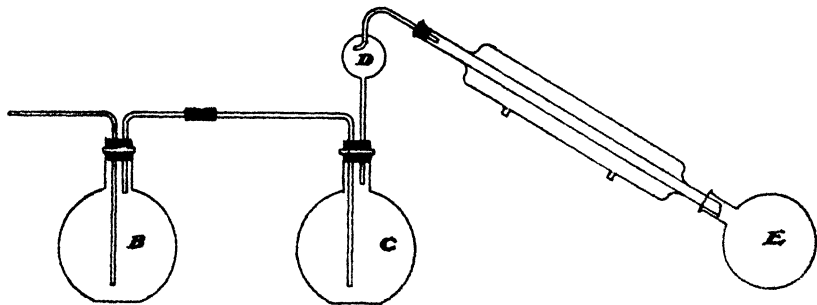
oxide may be present in small amounts with copper oxide." Later work on the part of the writer has convinced him that, while in a measure true, both of the above statements give an erroneous impression. In particular, I have never been able to detect more than minute traces of arsenic acid or cuprous oxide in any carefully prepared samples. However, the variation from Ehrmann's formula in the case of some samples is too great to be explained on the assumption of impurities present in the samples. The present paper presents an attempt to explain these variations and to throw light on the constitution of these important compounds.

#### EXPERIMENTAL, PART.

The analytical methods employed were as follows: The sample in which arsenic was to be determined was dissolved in the smallest possible amount of very dilute sulphuric acid, heating on the water-bath, if necessary. The resulting solution was titrated with standard iodine solution according to the method of the writer and Beans.<sup>1</sup> The presence of a tartrate as given in this method permits of the titration of arsenites containing zinc, nickel, or cobalt in solution as well as copper.

The copper determinations were made by electrolysis of samples from which the arsenic had practically all been volatilized by evaporating nearly to dryness on the water-bath with the addition of strong hydrochloric acid. The copper chloride was then converted into the nitrate by repeated evaporations with small quantities of nitric acid.

The volatile organic acids were determined by decomposing the green in a flask containing an acid potassium sulphate solution. The apparatus is as the following figure shows.



In B is placed an excess of potassium bisulphate. Steam free from carbon dioxide is passed into the apparatus till the distillate is neutral to phenolphthalein. The steam is then turned off, the sample inserted in B and the distillation continued till the distillate is neutral. Burners under B and C keep the condensation from accumulating in excessive quantity in the flasks. The flask C serves as a trap to retain traces of bisulphate, copper and arsenic. The distillate caught in E was titrated in the usual manner. Several determinations with zinc acetate gave results in accordance with the theory to the second decimal in percentages. The distillate from samples containing arsenious acid showed, in some cases, a faint trace of arsenic which, however, showed practically no acid reaction with phenolphthalein.

The greatest difficulty encountered in the work, and the only cause of uncertainty in the mind of the writer as to the accuracy of the conclusions, is the difficulty in distinguishing between mixtures and true compounds and in preparing the latter, since this class of bodies does not admit of purification by recrystallization. The microscope gives the most satisfactory evidence of the presence or absence of impurities. Free white arsenic and Scheele's green could be readily detected, even when present in minute quantities. The microscopic examination of Paris green is given very fully and clearly by Sattler.<sup>1</sup>

Samples of the green were made in nearly every possible way and several hundred were analyzed. Only such methods of preparation and such analytical data as seem to have a definite bearing on the problem at hand will be given in this paper.

*Formic Green.*—Formic acid was treated with freshly precipitated copper hydroxide in excess and filtered. The copper present in solution per cubic centimeter was determined. White arsenic was dissolved in sodium hydroxide by boiling, a drop of phenolphthalein added and dilute formic acid added drop by drop till the color was just discharged. The hot solutions of copper and arsenic were mixed in such proportions that 4 molecules of copper oxide were present for 3 molecules of arsenious oxide. The precipitate of Scheele's green was allowed to stand several days till converted into the characteristic brilliant green precipitate. The composition of this precipitate was as follows:

<sup>1</sup> Z. angew. Chem. 1, 35-47. (Not Z. anal. Chem. 11, 35, as given in Chem. News, 80, 261, and Stillman's "Engineering Chemistry," p. 422; Chem. Pub. Co., 1900.)

	Calculated for $3\text{CuAs}_2\text{O}_4 \cdot \text{CuC}_2\text{H}_3\text{O}_4$ Per cent.	Found. Per cent.
CuO .....	32.28	32.56
$\text{As}_2\text{O}_3$ .....	60.22	59.78
Formic anhydride .....	7.50	7.70

*Acetic Green.*—A sample prepared in the same manner as the formic, using acetic instead of formic acid, showed the following composition :

	Calculated for $3\text{CuAs}_2\text{O}_4 \cdot \text{CuC}_4\text{H}_7\text{O}_4$	Found. Per cent.
CuO .....	31.39	31.75
$\text{As}_2\text{O}_3$ .....	58.55	57.55
Acetic anhydride .....	10.06	10.31

A very large number of samples of acetic green, made in many different ways, with excess of copper, excess of acetic acid, excess of arsenic, or with an excess of any two of these, showed the presence of 57.3 to 57.7 per cent. of arsenious oxide. The highest result obtained on any sample that appeared free from uncombined white arsenic when examined under the microscope was 58.19 per cent.

*Propionic Green.*—I find no mention of this compound in the literature of the subject. In preparing it the method used in making the formic green was followed, except that an aqueous solution of white arsenic was used. The green formed was found to be impure under the microscope. Hence it was digested, first with an aqueous solution of white arsenic, then with a solution of sodium propionate. After this treatment all foreign substances seemed to be removed. The analysis gave:

	Calculated for $3\text{CuAs}_2\text{O}_4 \cdot \text{CuC}_6\text{H}_{11}\text{O}_3$ Per cent.	Found. Per cent.
CuO .....	30.54	30.37
$\text{As}_2\text{O}_3$ .....	56.98	56.66
Propionic anhydride .....	12.48	12.91

*Butyric Green.*—This green was made in the same manner as the formic green. The analysis gave:

	Calculated for		Analysis given by Wöhler <sup>1</sup>	Found.
	$3\text{CuAs}_2\text{O}_4 \cdot \text{CuC}_8\text{H}_{17}\text{O}_4$ Per cent.	$2\text{CuAs}_2\text{O}_4 \cdot \text{CuC}_8\text{H}_{17}\text{O}_4$ Per cent.	Per cent.	Per cent.
CuO .....	29.74	30.11	30.5	29.55
$\text{As}_2\text{O}_3$ .....	55.49	49.93	50.1	54.00
Butyric anhydride .....	14.77	19.96	19.4	16.33

<sup>1</sup> Ann. 94, 45.

While fully appreciating the difficulties of obtaining pure substances and the limits of analytical accuracy, these analyses seem to point clearly to the following:

Paris green and its homologues are compounds of copper meta-arsenite and a copper salt of the corresponding acid. The ratio most frequently approaches 3:1 but in some cases approaches 2:1. The crystalline structure within these limits and the color do not vary with the composition. Efforts to obtain compounds approaching the ratio of 4:1 or 1:1 were without result, as will be given later in this paper.

To study the effect of the nature of acids in determining the ratio of the copper arsenite and the copper organic salt, solutions of copper formate, acetate and propionate were so made up that the same quantities of copper were present in equal volumes (2.4683 grams CuO in 132 cc.). Exactly the same amount of sodium arsenite (see method of preparing formic green) was added in each case, and like conditions of temperature were maintained. The arsenic trioxide in each was as follows:

	Calculated for 3CuAs <sub>2</sub> O <sub>4</sub> Cu(acid) <sub>2</sub> . Per cent	Found Per cent	Variation.
Formic.....	60.22	59.23	0.99
Acetic.....	58.55	57.47	—1.08
Propionic.....	56.98	54.77	—2.21

It will be noted that all the figures for the arsenic are below the theory required for 3 of copper arsenite to 1 of copper organic salt, and that the propionic shows a rapid approach towards the ratio of 2:1 as Wöhler found in the butyric. In the same series of acids the stronger the organic acid the more nearly the ratio approaches 3:1. The rule holds true also in the chloracetic acid series which readily form greens.

	Calculated for As <sub>2</sub> O <sub>3</sub> Per cent	Found. Per cent	Variation.
Trichloracetic.....	48.64	47.27	—1.37
Monochloracetic.....	54.83	52.96	—1.87

*Green Containing a Dibasic Acid.*—All suggestions for structural formulas for Paris green that I am familiar with assume a more or less complicated chain with copper-linking arsenious complexes, terminating with a copper atom at each end, one of whose bonds is saturated with acetic acid. Since, however, acetic acid may be replaced by succinic, such a configuration becomes

improbable, since it involves the conception of a very complicated closed chain. The succinic green was prepared as the formic, and was found to contain 57.20 per cent. of arsenious oxide while the ratio of 3:1 would require 58.60 per cent.

In this connection it may be noted that apparently compounds of the type of Paris green may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and forms no complex ions with copper. I have not succeeded in forming greens under other conditions, though numerous attempts were made.

*The Action of Various Solutions on Paris Green.*—When Paris green of a composition approximately 3:1 is boiled with a solution of arsenious acid in very large excess, if the green be filtered off and dried, a product of more nearly exactly 3:1 in composition is obtained, but I have never been able to obtain a product having the physical properties of Paris green in which the percentage of arsenic trioxide was as high as 58.55 per cent. as the theory for 3:1 requires. If, however, the boiling be continued the green will suddenly become lighter colored and finally change to a blue-green-white product. By repeated treatment with boiling arsenious acid solution the green is converted into copper meta-arsenite.

	Analysis of sample. Per cent.	Calculated for $\text{CuAs}_2\text{O}_6$ . Per cent.
$\text{As}_2\text{O}_3$ .....	71.55	71.33
$\text{CuO}$ .....	28.59	28.67

This copper meta-arsenite was pseudomorphous after Paris green. I find no mention of anhydrous copper meta-arsenite in the literature of the subject. The same substance partially hydrated<sup>1</sup> can be made by treating copper hydroxide with an excess of a solution of arsenious acid, allowing to stand for several days, repeating the process and finally boiling for several hours.

## ANALYSIS.

	Per cent.
$\text{CuO}$ .....	28.30
$\text{As}_2\text{O}_3$ .....	70.13
$\text{H}_2\text{O}$ .....	1.57

The color is identical with the preceding. The substance is a gray crystalline powder. I was unable to combine copper meta-arsenite directly with copper acetate to form Paris green.

<sup>1</sup> Compare Stavenhagen: *J. nr. Chem.* [2] 51, 1

By treating Paris green with a neutral solution of copper acetate a brown amorphous powder, pseudomorphic after Paris green, is formed. It contains a higher percentage of copper and a lower percentage of the other constituents than Paris green and is always hydrated. By boiling Paris green with dilute acetic acid the green is slowly dissolved but no marked change in the composition of the undissolved part is to be detected.

*Action of Water on Paris Green.*—This action is of great practical interest, since soluble arsenic used as an insecticide burns foliage. Notwithstanding the work of several investigators<sup>1</sup> on the subject, Bulletin 151 of the California Experiment Station, p. 19, contains the following paragraph: "Examination by this Station's Laboratory Method.—This takes into account not only the limits of orchard practice with Paris green, but also reckons with the remarkable (?) properties ascribed to Paris green by some chemists when it is treated with plain distilled water; regardless of the fact that this article—acetarsenite of copper—as manufactured to-day, is instantaneously precipitated from complex solutions containing alkali and often excessive quantities of various acids."

A sample of apparently very pure green (composition nearly in the ratio 3:1) was finely pulverized and heated with five hundred parts of distilled water in a sealed tube. Of the original sample there passed into solution,

	Per cent.
CuO.....	6.46
As <sub>2</sub> O <sub>3</sub> .....	24.32
Acetic anhydride.....	9.27

A sample of the same was boiled for several hours with repeated changes of ammonia-free, carbonic acid-free distilled water. The undissolved portion was finally dried. It showed the following composition:

	Per cent.
Free CuO, not dissolved by cold dilute H <sub>2</sub> SO <sub>4</sub> .....	1.48
Combined CuO.....	49.35
As <sub>2</sub> O <sub>3</sub> .....	25.65
Water of hydration and traces of combined acetic acid not determined.....	.....

These figures seem to point out that "plain distilled water" in sufficient quantity would ultimately resolve Paris green into its component parts.

<sup>1</sup> Haywood: This Journal, 22, 705; Hilgard: Ibid. 22, 690; Avery and Beans: Ibid. 23, 111.

*Attempts to Prepare Compounds Analogous to Paris Green Substituting Other Metals for Copper.*—As much light had been thrown on the constitution of Paris green by the substitution of other acids for acetic, I endeavored to make similar compounds, using nickel, cobalt, cadmium and zinc in the place of copper. Only zinc gave definite crystalline products.

A solution of zinc acetate containing a little free acetic acid on the addition of an aqueous solution of arsenious oxide deposits a granular white powder, which, under the microscope, appears exactly like certain forms of Paris green except that the balls are white or colorless. The balls are frequently rougher than Paris green balls and the component parts are more easily seen. The individuals appear often in the form of figures  $g$ ,  $g_2$ ,  $h$ ,  $i$ ,  $i_2$  as given by Sattler.<sup>1</sup>

The composition of one sample was as follows:

	Calculated for ZnAs <sub>2</sub> O <sub>4</sub> . Per cent.	Found. Per cent.
ZnO.....	29.13	29.10
As <sub>2</sub> O <sub>3</sub> .....	70.87	70.13
Acetic anhydride.....	.....	0.75

Other samples showed as low a percentage of arsenic as 69.5 per cent., from which a higher percentage of acetic is to be inferred. The products, in my opinion, were zinc meta-arsenite crystallized in isomorphic mixtures with zinc acetate and in which the latter was present in small quantities. Zinc meta-arsenite, of which I find no mention in the literature of the subject, can be readily made by dissolving arsenious acid in sodium hydroxide, adding a drop of phenolphthalein, decolorizing with a little dilute sulphuric acid and adding to a hot solution of zinc sulphate. The crystals are of the form just described.

#### ANALYSIS OF SAMPLE.

	Per cent.
ZnO.....	28.95
As <sub>2</sub> O <sub>3</sub> .....	70.91

The precipitate was free from sulphates.

When zinc butyrate is substituted for zinc acetate and butyric for acetic acid, the precipitate formed by adding arsenious acid may contain as high as 10 per cent. butyric anhydride. In such cases, however, the precipitate is largely mixed with zinc ortho-

<sup>1</sup> Z. angew. Chem. 1, 37.



arsenite.<sup>1</sup> This higher percentage of the fatty acid, however, shows that butyric acid has a stronger tendency to replace arsenious acid in the zinc as well as in the copper compounds.

In conclusion, I would express my obligations to F. O. Woodruff for his carefully prepared bibliography which he placed at my disposal and to R. Corr and Fred Upson, of this laboratory, without whose careful work in preparing and analyzing compounds, only a small part of which are given here, this work could not have been brought to completion.

THE UNIVERSITY OF NEBRASKA.

## A NEW ANALYSIS OF THE WATER OF OWENS LAKE, CALIFORNIA.

BY C. H. STONE AND F. M. EATON.

Received June 30, 1906.

IN the eastern part of California between the White Mountain and Sierra Nevada Ranges, is a V-shaped depression, known as Owens Valley. Measured from crest to crest of the confining mountains, the valley is 10 to 25 miles wide and 125 miles long. The lowest part of the depression is occupied by a saline body of water called Owens Lake. This was originally described as having an area of about 110 square miles, with an average depth of 9 feet 10 inches. The only forms of life inhabiting the water are infusoria, alkali shrimps and the larvae of the alkali flies. There is no outlet, but the lake is fed by the Owens River and a number of small streams, practically all of which enter the valley from the Sierra side. While in the earlier reports it was stated that the loss by evaporation was very nearly counterbalanced by the inflowing water, evidences are abundant to-day that the size of the lake is decreasing. Mr. W. T. Lee, geologist of the U. S. Geological Survey, says in one of his recent bulletins: "The density of the water has increased to a point where sodium bicarbonate precipitates during the winter months without concentration by evaporation. From 1884 to 1894, the lake surface remained practically stationary; from 1894 to 1904 the surface has lowered 16 feet, decreasing the length of the lake by five miles and the width by about two miles."

Owens Lake is probably the largest natural soda deposit in the world. Thirty years ago, Loew estimated that it contained

<sup>1</sup> Bloxam: J. Chem. Soc. 15, 296 (1862).

22,000,000 tons of sodium carbonate. For the past twenty years, the Inyo Development Co. has had an extensive plant for the recovery of this soda at Keeler, so that the conditions have been under careful scrutiny for a long time. From time to time, partial analyses of this water have been made. A few are given below for comparison with our own work. To render such comparison easier they have all been recalculated into parts per million of the various ions. In so far as we know, all have been corrected for the specific gravity of the water.

## ANALYSES OF THE WATER OF OWENS LAKE, CALIFORNIA.

	Parts per million.			
	A.	B.	C	D.
Si.....	76.5	96.8	984.0	
Fe.....		9.2		
Al.....	trace	12.0		
Ca.....	trace	13.2		
Mg.....	trace	4.7		
K.....	2750.6	1548.0	1238.9	
Na.....	21652.1	26835.6	39032.4	83133.6
Li.....	trace			
SO <sub>4</sub> .....	9361.7	7066.7	9525.3	20572.4
Cl.....	13443.8	18214.3	25513.9	56090.0
CO <sub>3</sub> .....	13145.8	18265.2	23573.9	52465.5
PO <sub>4</sub> .....	trace			
B <sub>2</sub> O <sub>3</sub> .....	trace	345.6		4590.2
H.....		59.3		202.0
NO <sub>3</sub> .....	trace			
Organic matter.....	trace		242.2	
Total solids.....	60430.	72471.	100111.	217054.
Sp. gr.....	1.051	1.062 <sup>1</sup>		1.1861

"A."—Analysis by Oscar Loew, in 1876. See U. S. G. S. 8th Annual Report, page 295.

"B."—Analysis by T. M. Chatard, U. S. G. S., Bulletin 60. Samples taken September 17, 1886.

"C."—See "Saline Deposits of California," State Mining Bureau Bulletin, No. 24, 1902, page 95.

"D."—Analysis by N. Wrinkle, Manager of the Inyo Development Company's Works, at Keeler, Cal. Sample taken July, 1904.

The sample which we analyzed was collected by Mr. N. Wrinkle, superintendent of the Inyo Development Co., about 2,000 feet from the shore of the lake and at a depth of about 5 feet. As the

<sup>1</sup> At 25° C.

methods applied were necessarily different from those ordinarily used in water analysis, we have thought that a short description of them might be of interest.

Considering the small amounts of calcium, magnesium, phosphates, etc., shown in the above analyses, one's first thought naturally is that a large amount of the water must be evaporated in order to obtain enough of these substances to work with. But a second thought will show the futility of this for the water is already saturated and the evaporation of a large quantity is not only a difficult matter on account of the crust which forms over the surface of the liquid almost as soon as the dish touches the steam-bath, but also undesirable because of the enormous amount of salt to be handled. Therefore it was found desirable to follow the procedure of Mr. T. M. Chatard in his excellent study of this lake in 1886, and work on portions of 50 cc. to 100 cc. The specific gravity was found by the pycnometer method, each of us making the determination independently and arriving at identically the same result.

The question of total soluble salts was a troublesome one on account of the amount of water, both mechanically held and chemically combined, which must be expelled without driving off carbon dioxide. Being unable to secure an apparatus such as Chatard used we were obliged to devise a method of our own. Ten cc. of the water were evaporated to dryness in each of two platinum dishes; one of these was ignited at a low heat, weighed and the carbon dioxide in the residue determined gravimetrically. In the other, carbon dioxide was determined without previous ignition. Then having determined the carbon dioxide in the original water, it was easy to calculate the loss of the same due to evaporation and ignition. From these data the weight of the total solids with all water expelled may be derived.

We realize that this makes no allowance for organic matter, but this is negligible when compared with the weight of the solids found.

Another portion of 100 cc. was acidified, evaporated to dryness, and the silica dehydrated, filtered off and weighed. In the filtrate the iron and the alumina were precipitated by ammonia, but on account of the presence of phosphates it seemed probable that these phosphates and also calcium would be found in the

precipitate. Therefore we fused the latter with potassium acid sulphate and after solution determined the phosphoric acid, and tested for calcium with negative results. Deducting the weight of the phosphoric acid from the total weight of precipitate gave us the weight of the iron and alumina. In the filtrate from the ammonia precipitation the lime and magnesia were determined as usual.

In two other portions of 50 cc. each sulphuric acid was determined as barium sulphate and in the filtrate from this the total alkalies were determined in the usual way, using milk of lime and ammonium carbonate. In one of these the potash was determined with chlorplatinic acid. From the other, lithium was extracted with amyl alcohol according to the method of Gooch and Whitfield (Bull. 47, U. S. G. S.). Two such separations were made in order to insure the complete extraction of the lithium and the proper correction was applied for the volume of amyl alcohol used. The lithium was then converted to sulphate and weighed. This residue contained whatever rubidium, caesium and thallium were present in the water and qualitative tests were made for these according to methods given in Behren's "Microchemical Analysis." Phosphoric acid was determined in a separate portion of 50 cc. by precipitation with ammonium molybdate and finally with magnesia mixture, having first removed the arsenic with hydrogen sulphide. Carbon dioxide and chlorine were determined gravimetrically, the one by absorption in caustic potash and the other by precipitation with silver nitrate.

We first endeavored to determine nitrates by the Sprengel method, having previously removed the chlorine with silver oxide, but found on adding the phenolsulphonic acid that red fumes of nitrous oxide were freely evolved. In view of the large amount of nitrate present we were obliged to resort to another method. Twenty-five cc. of the water were diluted to 200 cc., 10 cc. of caustic soda added and the solution boiled until the volume was reduced to 70 cc. When cold, it was poured into a glass cylinder holding 120 cc., 20 sq. cm. of aluminum foil added and the mouth of the cylinder closed with a cork bearing a small tube filled with pumice moistened with hydrochloric acid. After standing several hours, the contents of the tube were transferred to a retort, caustic potash added and the ammonia distilled off and determined by titration.

Without expecting any particular results, hydrogen sulphide was passed into a portion of the water heated to boiling. To our surprise, a considerable yellow precipitate formed, and on examining this by the Marsh test it was found to be arsenic. This was then determined quantitatively in 100 cc. of the water by precipitation with hydrogen sulphide and finally with magnesia mixture. Every reagent used was tested for arsenic and several blanks were run, so that there is no reasonable room for doubt that the arsenic came from the water itself.

After attempting to determine the boric acid by the methods of Marignac and of Gooch, and having poor success with the former on account of the amount of salt in the water, and with the latter because of the difficulty in removing the chlorine, we finally adopted the following method: 100 cc. of the water were placed in a large Florence flask with 300-400 cc. of distilled water, the boric acid liberated by hydrochloric acid and then the flask was connected to a condenser and steam blown through it. In this way the boric acid was distilled over with the steam free from everything but hydrochloric acid and was received in a solution of caustic potash. A test made at the end of the operation showed that all the boric acid had passed over into the potash solution. Now the solution in the receiver, containing only potassium borate, potassium chloride and potassium hydroxide, was treated exactly as in Stromeyer's process save that Fresenius' modification for removing the silica was adopted.

The results of the analysis are given in the following table; all are expressed in parts per million, and are corrected for the specific gravity of the water.

Duplicates were run on all the determinations except lithium and boron, and the results checking very closely in all cases, they have been averaged for this table. The iron and alumina were calculated as alumina because of the small amount of the precipitate which seemed to be iron. The bicarbonates were determined by titration with sodium acid sulphate and found to be 7721 parts, calculated as  $\text{HCO}_3$ .

## OWENS LAKE.

## Averages.

Specific gravity .....	1.1954
Si.....	139.2
FeAl (calculated all as Al).....	47.5
Ca.....	33.8
Mg.....	14.9
K.....	3447.9
Na .....	81176.3
Li.....	56.8
SO <sub>4</sub> .....	21173.5
Cl .....	52898.0
CO <sub>3</sub> .....	52325.5
PO <sub>4</sub> .....	237.9
B <sub>4</sub> O <sub>7</sub> .....	296.4
H.....	130.2
As .....	83.8
NO <sub>3</sub> .....	947.7
Rb.....	trace
Cs.....	trace
<hr/>	
Total solids (by addition).....	213320.
Total solids determined.....	213661.
O <sub>2</sub> (for SiO <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> and As <sub>2</sub> O <sub>3</sub> )....	310.3

As will be seen from the table, sodium and potassium carbonates, chlorides and sulphates constitute by far the major part of the salts present in the water. The large amount of sulphate is important because this is the most troublesome salt to a manufacturer of soda. The arsenic is a curious and rather unexpected feature, for while it is often present in ground waters it is, we believe, seldom a constituent of surface waters. In this case it very probably arises from the decomposition of arsenopyrite. The amount of phosphate is another interesting feature; in previous analyses of water of the lake this has been reported simply as trace and in the majority of water analyses it is not determined at all. There are, we believe, few water analyses on record where the amount of phosphate reported is as great as in Owens Lake. Another noteworthy determination is that of nitrates. Of course the amount here reported may be exceeded in a few cases where the water percolates through nitrate beds, but this figure has rarely if ever been reached by a surface water. The carbonate is the feature of greatest commercial interest and is the largest we have ever found in a natural water, being over three times the amount present in the Big Soda Lake at Ragtown,

Nevada. It may be of interest to compare the chlorine found in Owens Lake with that present in various other saline waters. The average chlorine for the ocean is about 1900 parts per 1,000,000; Big Soda Lake has 40,000 parts; Great Salt Lake (in 1873) 73,000; Urmiah Lake, 120,000; Bogdo Lake, 160,000; Indevsk Lake, 160,000; Elton Lake, 170,000; the Dead Sea, in 1864, a maximum of 170,000; and two salt springs in Oklahoma, recently examined by one of us, over 180,000 parts. Thus it will be seen that all the above-named waters, with the exception of the ocean and Big Soda Lake, have a higher chlorine content than Owens Lake, and exactly the same relation holds with regard to the total solids.

While no general conclusions can be drawn from the results of a single analysis, this one has at least shown that the water of Owens Lake is rapidly concentrating and at the present rate will soon reach the saturation point. It has also demonstrated the existence in determinable quantities of certain substances which have hitherto been neglected. We believe that if a similar analysis could be made, at regular intervals, of several of the important saline bodies of water, such as Great Salt Lake, Owens Lake, Soda Lake, etc., interesting and valuable data would be accumulated, and it is our hope to be able to undertake a small portion of such work in the near future.

U. S. GEOLOGICAL SURVEY,  
BERKELEY, CAL.

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[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

## CHEMICAL AND PHYSIOLOGICAL EXAMINATION OF THE FRUIT OF CHAILLETIA TOXICARIA.<sup>1</sup>

(A WEST AFRICAN POISON.)

BY FREDERICK B. POWER AND FRANK TUTIN,

Received June 19, 1906.

THE present investigation of the fruit of *Chailletia toxicaria*, Don, was undertaken at the suggestion of Dr. W. Renner, Medical Officer, Colonial Hospital, Freetown, Sierra Leone, who also kindly provided us with the material for this purpose.

The interest which this subject possesses will be apparent from

<sup>1</sup> Presented, in abstract, at the International Congress of Applied Chemistry, Rome, Italy, April, 1906.

the following abstract of a paper published by Dr. Renner, entitled "Native Poison, West Africa."<sup>1</sup>

"For some years now, death by poison has been the subject of talk in the Colony of Sierra Leone, and one could scarcely credit the statements so often made with respect to this subject. No one, it would appear, dies from natural causes. Poisoning in one form or another is put down as the cause of death, not only among the poor but also among the rich, and yet no one would or could come forward to attest the fact that such a one had been poisoned by such a substance. Some of these deaths which appear to be mysterious have given cause for great alarm and anxiety, and aroused a feeling of dread and bitterness against the country doctors to whom they are attributed.

"A peculiar kind of disease, of the origin of which no account could be given, is now and again met with among the people. The European doctor, when called in, is puzzled, for he sees before him a young healthy man or woman, between the ages of twenty-three and forty years, struck down with paralysis. He examines the case carefully, cross-examines scrupulously the patient and his friends, and fails to arrive at any conclusion from these as to the source of the trouble. He suspects poison, and is told that the person has been poisoned. He endeavors to treat the symptoms, and either fails or the case is removed to a country doctor. The individual may recover or die, this depending on the nature and the quantity of the poison administered. These cases are brought forward daily. It has been my fortune lately to discover the cause of one of the mysterious and sudden diseases that affects the natives in the form of paralysis of the lower limbs."

A description is given by Dr. Renner of a case of poisoning, which occurred with a native laborer through his having eaten some fish on which the ground fruit of *Chailletia toxicaria* had been strewn for the purpose of killing rats, and the article then continues as follows:

"The *Chailletia toxicaria* belongs to the natural order of *Chailletiaceæ*, and is known as 'Ratsbane.' In the Colony proper it is called 'Broken Back.' By the Mendis of the Hinterland it is known under the name of 'Magbevi,' and by the Timnes as

<sup>1</sup> J. African Society, 1904, pp. 109-111. Compare also The British Medical Journal, June 4, 1904, p. 1314.



'Manäk.' It grows plentifully in West Africa and South America, and the fruit, which contains the poisonous substance, is used largely for the destruction of rats and other animals; but beyond this it is also used extensively by the people in the Colony and the Hinterland to poison one another. Conversing with some of the older men of the Timnes and Mendis, I found that with them it is very frequently used against their enemies to poison well-water or streams which supply hostile villages. Domestic animals poisoned by it are seen to rush about in great excitement as if in severe pain; they vomit, and drag their hind limbs, which ultimately become paralyzed. The forearm and chest muscles become paralyzed also, and they die from paralysis of the respiratory centre."

In the "Flora of Tropical Africa," by Daniel Oliver, F.R.S., London, 1868, Vol. I, p. 341, a complete description is given of the plant in question, from which the following, including references to its synonymy and habitat, is abstracted:

"*Chailletia toxicaria*, Don, DC. Prod. II, 57. A glabrous shrub or the young shoots and inflorescence mealy-puberulous at first. Leaves rather coriaceous . . . . .  $2\frac{1}{2}$ -6 inches long,  $1\frac{1}{4}$ - $2\frac{1}{4}$  inches broad, occasionally rather larger. Fruit  $1-1\frac{1}{2}$  inches long, ellipsoidal, hard and woody, one-celled, one-seeded.

"*Synonym.*—*C. affinis*, Planch. Fl. Nigrit 276.

"*Habitat.*—Upper Guinea, Sierra Leone, and Senegambia."

The "Treasury of Botany," by Lindley and Moore, London, 1899, Vol. I, p. 260, also gives a description of *Chailletia*, together with the following information:

"A genus which is found more or less in most tropical countries, but represented in greatest numbers in Brazil. The only extra-tropical species is *C. cymosa*, which is a native of South Africa; and the only species whose uses are recorded is *C. toxicaria*, a native of Sierra Leone, where the seeds of this plant are said to be used by the colonists for poisoning rats and by them called ratsbane. Upwards of thirty species are known."

The above-mentioned *Chailletia cymosa* is of special interest in this connection, as will be evident from the following notice of it recorded in the "Bulletin of the Imperial Institute," 1903, Vol. I, p. 14. "Preliminary experiments have shown that the leaves furnish prussic acid when powdered and moistened with

water, and from them a cyanogenetic glucoside has been isolated, and is being further examined."

A description of this species of *Chailletia* is given in the "Flora Capensis," by Harvey and Sonder, Dublin, 1859-1860, Vol. I, p. 450, from which the following is abstracted:

"*Chailletia cymosa* (Hook.  *Ic. Pl.* t. 591). Habitat, Aapges River, Burke and Zeyher! Oct. (Herb. Hook., T. C. D.). A very dwarf shrub or suffrutex, under a foot in height. Leaves 3-3½ inches long, 6-10 lines wide, etc. Fruit unknown. A remarkable plant, very different in habit from others of the genus, but apparently not differing generically, unless the fruit afford a character."

#### EXPERIMENTAL.

The material received by us from Dr. Renner, of Sierra Leone, corresponded with the description of the fruit of *Chailletia toxicaria*, Don, as recorded in Oliver's "Flora of Tropical Africa,"<sup>1</sup> with the exception that it is occasionally two-celled and two-seeded. This is also the case with authentic specimens of these fruits in the Museum of Economic Botany at Kew. The weight of the individual dry fruits ranges from about 5 to 8 grams.

The following preliminary experiments were conducted.

*Test for Alkaloid.*—Ten grams of the powdered fruit were digested with Prollius' fluid, and the resulting liquid filtered and evaporated. The residue, extracted with acidulated water, afforded no reaction with the usual alkaloid reagents.

*Test for a Cyanogenetic Glucoside.*—As it has been observed by other investigators<sup>1</sup> that the leaves of *Chailletia cymosa* contain a cyanogenetic glucoside, the fruit of *C. toxicaria* was specially tested for a substance of this class. Ten grams of the ground fruit were mixed with a little water and allowed to stand in a tightly corked flask for about twenty-four hours. As no odor of hydrocyanic acid was then apparent, an emulsion of sweet almonds was added, but this produced no evident change. The liquid was finally distilled, and the complete absence of hydrocyanic acid in the distillate was established by chemical tests. It could, therefore, be concluded that the fruit of *Chailletia toxicaria* does not contain a cyanogenetic compound, and this conclusion was confirmed by the more complete examination of

<sup>1</sup> Loc. cit.

a very much larger quantity of the fruit, which will subsequently be described.

*Test for a Poisonous Proteid.*—It was considered possible that the poisonous action of the fruit might be due to a proteid substance, such, for example, as ricin, abrin or robin. Fifty grams of the ground fruit were therefore digested with water at the ordinary temperature for three days, when the mixture was brought upon a strainer, expressed, and the liquid filtered. The clear filtrate afforded, however, no reaction for a soluble proteid.

*Extraction with Solvents.*—In order to obtain some further preliminary information respecting the character of the drug, 100 grams of it, in fine powder, were extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract obtained, after drying in a steam-oven until of constant weight, were as follows:

	Per cent
Petroleum (b. p. 40–60°) extracted	2.00
Ether	0.26
Chloroform	1.10
Ethyl acetate	3.04
Alcohol	6.84

Total, 12.24

For the purpose of a systematic examination of the constituents of the *Chauletia* fruit, 3000 grams of it, ground to a fine powder, were first extracted in a percolator with cold light petroleum, and subsequently with hot alcohol.

#### A. EXAMINATION OF THE PETROLEUM EXTRACT.

This was a yellowish brown fat, which, at ordinary temperatures, consisted of a mixture of an oily substance and a granular solid, but when exposed to cold became almost completely solid. The total amount of fatty matter was 55 grams, corresponding to 1.83 per cent. of the weight of the fruit. The solid was separated from the oil by filtration at the pump, then dissolved in hot acetone, some alcohol added, and the solution allowed to stand for a time. A little fluffy matter first separated, which was removed, and the fat was then deposited in the form of white nodules. These were separated by filtration, washed with alcohol, dried on a tile, then dissolved in a large quantity of absolute alcohol, in which they were sparingly soluble, and the solution filtered. When the liquid was nearly cold, the fat separated in white, crystalline

nodules, which were removed by filtration. After drying on a tile, a portion was finally dried in a vacuum desiccator, when it melted at 42-43°. Another portion was dried by heating in a steam-oven, when, after solidification, it melted at 35-40°. The whole of the substance was then recrystallized from absolute alcohol, when it melted sharply at 43°. Its solution in chloroform readily absorbed bromine.

0.1450 gram gave 0.4072 gram  $\text{CO}_2$  and 0.1571 gram  $\text{H}_2\text{O}$ .  $\text{C}=76.6$ ;  $\text{H}=12.0$ ;  $\text{C}_3\text{H}_5 \cdot (\text{C}_{18}\text{H}_{35}\text{O}_2)_2 \cdot \text{C}_{18}\text{H}_{33}\text{O}_2$  requires  $\text{C}=77.0$ ;  $\text{H}=12.1$  per cent. 0.2499 gram absorbed 0.0686 gram I. Hence the iodine value = 27.5.

This crystalline substance was evidently *oleodistearin*, which has a calculated iodine value of 28.6, and is stated to melt at 44°.¹ Further proof of its identity was afforded by the following experiment: 1.6 grams of the substance were hydrolyzed with an alcoholic solution of potassium hydroxide, and the acids thus obtained were fractionally crystallized many times. The most readily soluble fraction consisted of an oil which was found to be unsaturated, on treatment with nitrous acid formed a solid mass, and therefore consisted of oleic acid. The other fractions melted at 69-70°, and consisted entirely of stearic acid, as shown by the following analysis:

0.1049 gram gave 0.2912 gram  $\text{CO}_2$  and 0.1198 gram  $\text{H}_2\text{O}$ .  $\text{C}=75.7$ ;  $\text{H}=12.7$ ;  $\text{C}_{18}\text{H}_{30}\text{O}_2$  requires  $\text{C}=76.0$ ;  $\text{H}=12.7$  per cent.

The identification of the mixed triglyceride, oleodistearin, as a constituent of the fatty oil from *Chaillietia* fruit is of considerable interest, inasmuch as the number of substances of this class that have been isolated from either vegetable or animal fats and definitely characterized is comparatively small (compare Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes," third edition, Vol. I, p. 14).

The original filtrate from the granular solid which afforded the oleodistearin consisted of a brownish oil, which became partially solid on cold days. This, together with the fatty matter contained in the first and second mother-liquors from the recrystallization of the oleodistearin, was hydrolyzed by boiling with an alcoholic solution of potassium hydroxide. The alcohol was then removed, the alkaline residue mixed with clean sand, dried, and extracted in a Soxhlet apparatus with light petroleum. On

¹ Ber. 32, 388 (1899). Compare also Chem. Centr. 1, 1716 (1905).

removing the petroleum from this extract a dark brown resinous residue was obtained, which was dissolved in much alcohol, and the liquid boiled with animal charcoal and filtered. On cooling, a small quantity (about 0.5 gram) of a substance was deposited in the form of crystalline plates. This was removed by filtration, recrystallized several times from ethyl acetate, and then from ordinary spirit, in which it was very sparingly soluble. It was then almost colorless, and, after drying at  $100^{\circ}$ , melted at  $138-143^{\circ}$ . After again crystallizing from spirit, and drying at  $100^{\circ}$ , when it appeared to lose some water of crystallization, it softened and gradually melted at  $135-148^{\circ}$ .

0.0854 gram, dried at  $100^{\circ}$ , gave 0.2630 gram  $\text{CO}_2$  and 0.0952 gram  $\text{H}_2\text{O}$ .  $\text{C} = 84.0$ ;  $\text{H} = 12.4$ ;  $\text{C}_{28}\text{H}_{44}\text{O}$  requires  $\text{C} = 83.9$ ;  $\text{H} = 11.8$  per cent.

This substance was evidently a *phytosterol*, since it also afforded the color reactions characteristic of the latter when dissolved in chloroform and treated with acetic anhydride and sulphuric acid. As the melting-point was not sharp, it was possibly a mixture of substances of that class, but the amount was too small to admit of a further separation.

The alkaline mixture with sand, from which the *phytosterol* had been extracted, was treated with hot water in order to dissolve the potassium salts, the solution then acidified with sulphuric acid, and distilled in steam. A clear distillate was obtained, containing only a small amount of acids, which, after converting into their barium salts, were found to consist chiefly of *formic acid* with a little *butyric acid*. The non-volatile acids remaining in the flask were removed by shaking the liquid repeatedly with ether. The ethereal liquid was washed with water, dried with calcium chloride, the ether then removed, and the residue dissolved in hot spirit. After as much as possible of the solid acids had been removed by crystallization, the oily acids which separated from the mother-liquors were redissolved in alcohol and completely precipitated as lead salts by the addition of a solution of lead acetate in dilute alcohol. These lead salts were collected on a filter, washed with alcohol, dried, and then extracted with ether, when the greater portion dissolved. From the portion of lead salts which remained undissolved by this treatment the acids were regenerated, and; being solid, they were added to the above-mentioned solid acids which had previously

been separated by crystallization. The whole was then fractionally crystallized, when the most sparingly soluble fractions were found to consist of *stearic acid* (melting-point  $69^{\circ}$ ), while the more readily soluble ones appeared to be a mixture of stearic and palmitic acids, and melted at  $53\text{--}60^{\circ}$ .

From the above-mentioned portion of the lead salts which had been dissolved by ether the acids were likewise regenerated. An oily liquid was thus obtained, a portion of which, when treated with nitrous acid, became converted into a solid mass, thus indicating the presence of *oleic acid*. The remainder of this liquid was distilled under diminished pressure, when a pale yellow oil was obtained, from which no solid matter separated.

0.2508 gram absorbed 0.2696 gram I. Hence the iodine value = 107.5.

As oleic acid has a calculated iodine value of 90.1, it was evidently associated with some acid possessing a higher degree of unsaturation.

#### B. EXAMINATION OF THE ALCOHOL EXTRACT.

It has already been stated that the *Chaillietia* fruit, after having been extracted with light petroleum, was extracted with hot alcohol. This alcoholic extract was concentrated and mixed with water, in order to precipitate the resin. The mixture was warmed to expel the remaining alcohol, allowed to cool, and the insoluble resinous substance removed by filtration, washed with hot water and dried.

I. *The Resin*.—This formed a dry, brown, amorphous powder, having an odor somewhat resembling that of chocolate. The amount of resinous substance was 76 grams, corresponding to 2.5 per cent. of the weight of the fruit. It appeared to be slightly soluble in water, as a further quantity was deposited on concentrating the aqueous liquid. After keeping for some time it lost its original smell, and became much more sparingly soluble in alcohol. In order to ascertain whether any definite substance could be obtained from it, it was mixed with prepared sawdust, and extracted successively in a Soxhlet apparatus with chloroform, ethyl acetate, and alcohol. The amounts of extract obtained by these solvents, after drying in a steam oven, were as follows:

(a) *Chloroform Extract*, consisting of a dark green, soft resin, 11.83 grams.

(b) *Ethyl Acetate Extract*, a yellowish brown, very sticky resin, 4.30 grams.

(c) *Alcohol Extract*, a nearly hard, brown resin, 9.40 grams.

These results showed the resin to consist of a complex mixture, and, as after the final extraction with alcohol about two-thirds of the original substance remained undissolved in the form of a brown powder, it was evident that it had undergone some change, either in drying or in the process of extraction. As there appeared to be nothing crystalline in these products, they were not examined chemically, but were reserved for physiological tests.

II. *The Aqueous Liquid*.—The liquid from which the above-described resinous substances had been separated had a brownish color, gave a black coloration with ferric chloride, a dense, grayish colored precipitate with basic lead acetate, and reduced Fehling's solution. In order to purify it, basic lead acetate was added until no further precipitate was produced. This precipitate was collected by filtration at the pump, washed with a little water, and then suspended in water and decomposed by hydrogen sulphide. The filtrate from the precipitated lead sulphide formed a clear, dark brown liquid, which was concentrated under diminished pressure. A thick, dark brown syrup was thus obtained, which consisted chiefly of tannic and coloring-matters, and deposited nothing crystalline, even after long standing.

The aqueous filtrate from the basic lead acetate precipitate was completely deprived of lead by means of hydrogen sulphide, and then concentrated under diminished pressure to the consistency of a thick syrup. When heated with potassium hydroxide it evolved ammonia, and it readily reduced Fehling's solution. An aqueous solution of the syrup was slightly levorotatory, and afforded an osazone melting at  $214^{\circ}$ . The sugar, therefore, appeared to be chiefly *i-glucose*, the osazone of which is stated to melt at  $217-218^{\circ}$ .

#### PHYSIOLOGICAL TESTS AND ATTEMPTS TO ISOLATE THE POISONOUS PRINCIPLE.

The indefinite character of the products obtained from the original alcoholic extract *B*, as above described, rendered it important at this stage of the investigation that we should ascertain

which of them represented or contained the poisonous principle. For this purpose some physiological experiments were conducted for us, with essentially the following results.

I. *The Resin*.—The three extracts obtained from this by successive treatment with different solvents, as previously described, were separately tested. In each case 0.5 gram of the extract was administered to a small dog.

(a) *Chloroform Extract*.—This, after some hours, produced narcosis, and ultimately death, but did not cause the delirium and epileptiform convulsions which are such characteristic features of the poisonous action of *Chaillletia* fruit.

(b) *Ethyl Acetate Extract*.—This produced the characteristic convulsions, thus differing in its action from the preceding extract.

(c) *Alcohol Extract*.—This caused nausea, but no toxic symptoms.

II. *The Aqueous Liquid*.—This liquid, from which the above-mentioned resinous substances had been separated, and which had been further purified by means of basic lead acetate, was found to be highly toxic. When concentrated to a syrupy consistency it amounted to about 200 grams. Of this syrup 0.5 gram was administered to a dog, when after an interval of three hours the characteristic convulsions occurred, which were followed by death within fifteen minutes. The decomposed lead acetate compound was also toxic, and when given in the same amount as the syrup produced a similar effect, although somewhat more slowly. This result, however, was probably due to the occlusion of some of the aqueous liquid with the lead acetate precipitate, as the latter did not permit of being very thoroughly washed.

The preceding physiological experiments having shown that the syrupy aqueous liquid possessed in a high degree the poisonous properties of the *Chaillletia* fruit, and as nothing crystalline separated from it, even after standing for several weeks, an attempt was made to isolate the toxic principle by further treatment. The syrup was accordingly mixed with prepared sawdust, the mixture thoroughly dried in a vacuum over sulphuric acid, then brought into a Soxhlet apparatus, and extracted for two days with dry ethyl acetate. This removed a quantity of substance which was only sparingly soluble in the ethyl acetate, for it separated from the hot liquid as a brownish syrup. The liquid



decanted from the latter was concentrated to a small volume, when another portion of syrup separated, which was removed. From the remaining liquid the ethyl acetate was for the most part distilled off, when from the resulting syrup an exceedingly small quantity of a colorless, crystalline substance separated in the form of needles. The syrup containing these needles was diluted with a little alcohol and filtered, and a very small amount of the crystalline substance was thus obtained. This was only sparingly soluble in ethyl acetate and in alcohol, and practically insoluble in water. After recrystallization from hot alcohol, and drying at  $100^{\circ}$ , it melted at  $245-247^{\circ}$ , and left no ash on ignition. The amount of this substance was much too small for further chemical examination, but it was found to possess no marked physiological action, and evidently did not represent the toxic principle of the fruit.

The syrup from which the ethyl acetate liquid was first decanted represented the greater part of the substance extracted by this solvent. It readily reduced Fehling's solution, yielded a crystalline osazone melting at  $211-212^{\circ}$ , and evidently consisted largely of *i*-glucose.

It was subsequently ascertained, by physiological tests, that the syrup which separated from the ethyl acetate extract was devoid of toxic properties. A small portion of the sawdust, containing the substance which had been subjected to prolonged extraction with ethyl acetate, was then extracted with water, and, as this extract still possessed a high degree of toxicity, it was manifest that the ethyl acetate had removed practically none of the poisonous principle.

With consideration of these results, the dried mixture with sawdust was afterwards extracted for one day in a Soxhlet apparatus with absolute alcohol. The liquid in the flask deposited a quantity of syrup, from which the alcohol was decanted, and as from the latter, on further concentration, an additional quantity of syrup separated, this was also removed from the alcoholic liquid. These preparations, together with an aqueous extract of the sawdust remaining in the extraction apparatus, were all physiologically tested. They were all highly toxic, did not differ appreciably in their action, and nothing crystalline could be obtained from them.

The preliminary examination of *Chailletia* fruit having shown

the absence of an alkaloid, and, as so many non-alkaloidal, poisonous substances are glucosides, it was thought probable that the active constituent of the aqueous extract was also a substance of this nature. With the hope of obtaining some confirmation of this view, it was sought to ascertain whether it would yield any definite hydrolytic product. The material contained in the Soxhlet apparatus was, therefore, extracted with water, and in this liquid were dissolved the syrups obtained by the previous extraction with absolute alcohol. The whole was first shaken out several times with ether, which, however, removed only a trace of a brownish, syrupy substance. Sufficient hydrochloric acid was then added to make an approximately 5 per cent. solution, and the mixture boiled for three hours in a flask with an inverted condenser. During the boiling a large quantity of a black amorphous resin separated, and the entire mixture was subsequently distilled in steam. The first drops that passed over were slightly turbid, and had a somewhat empyreumatic odor, but no aldehyde or ketone could be detected in the distillate. The residue in the distilling flask was allowed to cool, and repeatedly shaken with ether. This did not dissolve the black resin, but removed a small quantity of a brownish syrup, which had an unpleasant odor, and, on the addition of water, separated a sticky resin. All the attempts to isolate the toxic principle, or to obtain some definite derivative of it, were, therefore, unsuccessful.

#### SUMMARY AND CONCLUSIONS.

The results of the investigation of the fruit of *Chailletia toxicaria*, Don, as detailed in the preceding pages, may be briefly summarized as follows:

A preliminary examination showed the fruit to contain no alkaloid, cyanogenetic glucoside, or soluble proteid, to which its highly poisonous properties could be attributed. The possible presence of a cyanogenetic glucoside was particularly considered, in view of the recorded statement that such a substance has been isolated from the leaves of the South African species, *Chailletia cymosa*, Hook.<sup>1</sup>

On extracting 3000 grams of the fruit with light petroleum (boiling-point 40–60°), 53 grams, or 1.83 per cent. of a yellowish

<sup>1</sup> Compare "Bulletin of the Imperial Institute," 1903, Vol. I, p. 14.

brown fat were obtained. From this a quantity of the mixed triglyceride, *oleodistearin*,  $C_8H_8.(C_{18}H_{35}O_2)_2.C_{18}H_{33}O_2$ , melting-point  $43^\circ$ , was directly separated, and from the residual fatty matter, after hydrolysis with an alcoholic solution of potassium hydroxide, the following substances were isolated: (1) A small quantity of a *phytosterol*,  $C_{28}H_{44}O$ , or possibly a mixture of substances of this class, melting at  $135-148^\circ$ ; (2) *Stearic* and *oleic acids*, the latter being apparently associated with an acid having a higher degree of unsaturation; (3) Very small amounts of *formic* and *butyric acids*.

The alcoholic extract of the fruit which had previously been deprived of fatty matter, when concentrated and mixed with water, yielded a quantity (76 grams) of *resinous substance* corresponding to 2.5 per cent. of the weight of the fruit. This consisted of a complex mixture, from which nothing crystalline could be obtained. By successive extraction with chloroform, ethyl acetate, and alcohol it was, however, resolved into products which differed essentially in their physiological action. The chloroform extract, for example, had a narcotic or paralytic effect, while the ethyl acetate extract produced delirium and convulsions, and the alcohol extract, although causing nausea, was not distinctly toxic.

The aqueous liquid, separated from the above-mentioned resinous substance, and deprived of tannic and coloring-matters, when concentrated under diminished pressure, formed a thick syrup, which contained a large amount of *glucose*. This syrup was extremely poisonous, producing, when administered to a dog in relatively small doses, the characteristic action of the fruit, *viz.*, delirium and epileptiform convulsions, soon followed by death. Although many attempts were made to separate the poisonous principle from the syrup by extracting the latter with various solvents, such as ethyl acetate, absolute alcohol, etc., these were unsuccessful, as all the liquids which were capable of removing the active principle also dissolved considerable amounts of sugar.

The physiological experiments connected with this investigation have led to the observation that, with the lower animals, the effects of the poison contained in the *Chaillietia* fruit are only manifested some time after its ingestion. According to the amount administered, a period of several hours may elapse before

the occurrence of the characteristic convulsions, but, after the onset of the symptoms, death usually follows within fifteen to thirty minutes. A *post-mortem* examination of the animal shows a condition of cerebral congestion and thrombosis of the superior longitudinal sinus.

It was considered possible that the narcotic effects produced by the chloroform extract of the resin, and the delirium and convulsions caused by the aqueous extract, as above described, are due to the same substance, and that the difference in the symptoms may depend upon the amount of the poison administered or the rate of its absorption. In order to test this assumption successive sub-toxic doses were given to a small dog during a period of several days. Nothing of a definite nature occurred until the tenth day, when the characteristic delirium commenced, followed shortly by convulsions, and death then ensued within about one hour. The *post-mortem* examination showed a condition of cerebral congestion, and a small patch, apparently of cortical necrosis, near the right crucial sulcus. These experiments thus permit of the following deductions:

(1) That the fruit of *Chaetelia toxicaria* contains at least two active principles, one of which causes cerebral depression or narcosis, and the other cerebral excitation, leading to epileptiform convulsions.

(2) That the poison which causes convulsions is very slowly excreted, so that a cumulative effect is produced by the administration of a series of individually innocuous doses.

It may finally be stated that all the physiological experiments required in the course of this investigation were conducted in the Wellcome Physiological Research Laboratories by Mr. H. H. Dale, and our best thanks are due to him for the valuable assistance he has given us.

## ON THE ACTION OF ACID CHLORIDES ON MIXTURES OF AMINES.

BY F. B. DAINS.

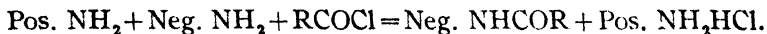
Received July 5, 1906.

IN the course of an investigation on the action of acid chlorides on ureas of the type  $RNHCSNHR'$ , the question arose, which an effort was made to answer, whether when a mixture of two

amines was treated with an acid chloride, any preference would be shown as to the amine attacked, and if so what the conditions were that would govern it. Thus given a molecular mixture of two amines and an acid chloride, there might be obtained as products, first the acyl derivatives of the two amines plus the hydrochlorides of the two amino bodies, and second the acyl derivative of one amine plus the salt of the other, a condition which can be represented as follows:



The results thus far obtained in this investigation point to the general conclusion, that when there is any appreciable difference in basicity between the two amines, there will be formed largely or altogether the acyl derivative of the more negative amine and the salt of the more positive one.



The terms positive and negative are used in a somewhat restricted sense, referring only to the ease of replacement of the hydrogen atom, since the results from this standpoint may not always agree with those obtained in other ways. Thus from the measurement of the electrical conductivity monoethylamine is a stronger base than ammonia, yet it is found that an amino hydrogen atom of ethylamine is more easily replaced than the hydrogen atom of ammonia.

#### EXPERIMENTAL.

The experimental work was done under two general conditions, either dissolving molecular quantities of the two amines in a neutral solvent like benzene or ether, and then adding the acid chloride either alone or diluted with the same solvent; or suspending the amines in a relatively large volume of water and then adding the acid chloride as in the usual Baumann-Schotten reaction.

Without making quantitative measurements, it seemed as if the reaction proceeded more rapidly and smoothly under these conditions than when caustic soda was used to combine with the hydrochloric acid set free. In the majority of cases the hard granular acyl derivative formed almost immediately, while the hydrochloride of the amine remained in solution when water was used.

*Ammonia and Primary Amines.*—Ammonia, if not in too great excess, can be used to combine with the free acid in the formation of benzoyl derivatives of primary amines giving a smooth and rapid reaction.

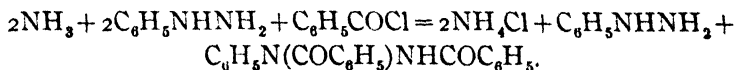
*Ammonia and Ethylamine.*—One molecule of ammonia and one molecule of monoethylamine were dissolved in an excess of water and one molecule of benzoyl chloride added with shaking. An oil was formed which was very soluble in alcohol and which, on standing, slowly solidified to long needles of ethylbenzamide (melting-point  $67^{\circ}$ ). The solution contained ammonium chloride.

*Ammonia and Aniline.*—Benzoyl chloride gave, with molecular proportions of ammonia and aniline, a hard granular precipitate of benzanilide, and ammonium chloride.

*Ammonia and o-Toluidine.*—These amines gave, in water solution with benzoyl chloride, easily and smoothly *o*-benztoluide and ammonium chloride.

*Ammonia and m-Brom-p-toluidine* yielded under the above conditions ammonium chloride and benzoic *m*-brom-*p*-toluide.

*Ammonia and Phenylhydrazine.*—Benzoyl chloride was added to the above amines in water solution. The substances reacted quickly and on examining the products formed, there were discovered ammonium chloride, phenylhydrazine, and dibenzoylphenylhydrazine. The course of the reaction can be represented as follows:



The first action of the acid chloride is to form the monobenzoylphenylhydrazine, but as this has still a second replaceable hydrogen atom and is more negative than either the ammonia or the phenylhydrazine, this hydrogen atom is substituted by the second benzoyl group giving the dibenzoylphenylhydrazine.

*Aniline and Other Primary Amines.*—Aniline, the simplest of the aromatic amines, affords a convenient standard of comparison in its reactivity with other amino bodies as to their relative positive or negative nature. Thus, where the second amine is more positive the products are an acyl anilide and the salt of the second amine. This has already been shown to be the case with ammonia and aniline.

*Aniline and Ethylamine.*—With molecular proportions of

ammonia, ethylamine and benzoyl chloride in water solution, the products were ethylamine hydrochloride and benzanilide.

*Aniline and o-Toluidine.*—Acetyl chloride gave with these substances in benzene solution acetanilide and a precipitate of *o*-toluidine hydrochloride. When acetic anhydride was added to a molecular mixture of aniline and the toluidine, the reaction product yielded, on investigation, acetanilide and *o*-toluidine, a result wholly in accordance with the action of the acetyl chloride.

When succinyl chloride was added to the aniline and *o*-toluidine suspended in water, the solid product formed consisted only of succinilide; no trace of succintoluide was discovered, a result which corresponds to the action of the more simple acid chlorides.

These same two amines in benzene solution gave with benzoyl chloride mainly benzanilide and *o*-toluidine hydrochloride, while small amounts of *o*-benztoluide and aniline were also identified.

*Aniline and p-Toluidine.*—When acetyl chloride is added to a solution of aniline and *p*-toluidine in benzene, much heat is evolved and the solution contains acetanilide and the hydrochloride of *p*-toluidine.

*Aniline and Pseudocumidine* yield with acetyl chloride in benzene solution acetanilide and pseudocumidine hydrochloride.

*Aniline and Phenylhydrazine.*—The aniline and phenylhydrazine were suspended in water and benzoyl chloride added. The results were entirely in harmony with the preceding, benzanilide and the salt of phenylhydrazine being formed.

The second series of amines includes those that are more negative than aniline, giving as general products, more or less completely, aniline hydrochloride and the acyl derivative of the second amine.

*Aniline and m-Nitroaniline* were suspended in a large excess of water and benzoyl chloride added. The solid product proved to be the benzoyl derivative of *m*-nitroaniline, while the filtrate contained aniline hydrochloride and a little *m*-nitroaniline.

In benzene solution these amines gave mainly *m*-nitroacetanilide and the hydrochloride of aniline.

*Aniline and p-Bromaniline.*—In benzene solution the chief products with benzoyl chloride were *p*-brombenzanilide and

aniline hydrochloride. A little *p*-bromaniline and traces of benzanilide were also isolated.

*Aniline and m-Brom-p-toluidine.*—The amines suspended in water yielded with benzoyl chloride benzoic *m*-brom-*p*-toluide, and aniline hydrochloride.

*Aniline and o-Anisidine.*—Benzoyl chloride gave with the above as main products aniline hydrochloride and the benzoyl derivative of *o*-anisidine. A little benzanilide was also isolated.

*Aniline and p-Phenetidine.*—These give, either in water or benzene solution, mixtures of products, with the benzoyl-*p*-phenetidide predominating.

*Aniline and m-Xylidine.*—Like the preceding, aniline and *m*-xylidine tend to give with benzoyl chloride, when suspended in water, a mixture of products. The benzoyl-*m*-xylide, however, is in excess, while the filtrate contains the salts of aniline and some *m*-xylidine.

In comparison with aniline, a much greater proportion of the acyl *m*-xylide is obtained than with other methyl derivatives like *o*- and *p*-toluidines, and pseudocumidine, which are more positive to aniline.

*Aniline and  $\alpha$ -Naphthylamine.*—These amines in benzene solution give with acetyl chloride chiefly  $\alpha$ -acetnaphthalide and aniline hydrochloride, while in water solution with benzoyl chloride, there are obtained largely benzoic  $\alpha$ -naphthalide and the aniline salt.

*Aniline and  $\beta$ -Naphthylamine.*—Acetyl chloride gave with these amines in benzene solution primarily acet- $\beta$ -naphthalide and aniline hydrochloride, together with some  $\beta$ -naphthylamine.

*o- and p-Toluidine.*—In one experiment in ether solution with acetyl chloride *p*-acettoluide and *o*-toluidine were obtained, but in another case with benzoyl chloride a mixture of the two benzotoluides resulted. The effect of the *o*-, *m*- and *p*-positions on the reaction will be investigated further.

*Pseudocumidine and m-Xylidine.*—These bodies when dissolved in benzene and treated with benzoyl chloride yielded the hydrochloride of pseudocumidine and benz-*m*-xylide, a result in accordance with their relative action toward aniline.

*Aniline and Monomethylaniline.*—Benzoyl chloride in water solution gave with these substances aniline hydrochloride, benzanilide, and an oily product which possibly contains some benzoyl-



monomethylaniline, but it has not as yet been obtained in a pure enough state for identification.

*Aniline and Diphenylamine.*—Molecular quantities of these amines yield in benzene solution benzanilide, aniline hydrochloride, diphenylamine and unchanged benzoyl chloride.

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## PIPERONAL AND HYDROGEN CHLORIDE: A TWO-COMPONENT THREE-PHASE SYSTEM.

BY F J MOORE

Received June 7, 1906.

SINCE it appears from a recent paper by D. McIntosh,<sup>1</sup> that he is also studying the action of the halogen acids upon aldehydes, the following extremely incomplete observations are communicated at this time to avoid any possibility of collision.

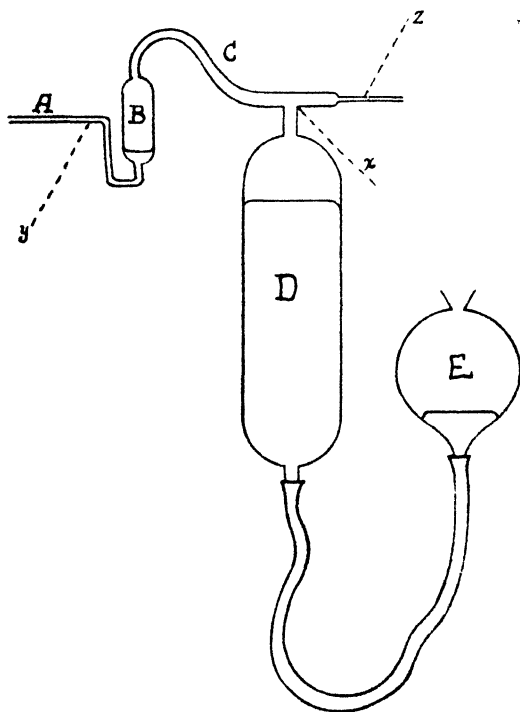
While investigating the action of some organic compounds upon piperonal, the accidental observation was made that this substance liquefies when brought into contact with dry hydrogen chloride. When the liquid thus formed was exposed to the air on a watch-glass, crystals appeared. A melting-point determination showed that these consisted of piperonal. The explanation of these phenomena obviously is, that piperonal adds hydrogen chloride as long as the pressure of the latter upon its surface is about one atmosphere, but the vapor pressure of the product is so great that when the partial pressure of the hydrogen chloride falls, all the gas is liberated. In order to bring out these relations more clearly, the apparatus was devised which is represented in the accompanying diagram.

B is a small bulb about 35 mm. high and 7 in diameter—outside measurement. D is a much larger cylinder about 135 mm. long and 40 in diameter. E is a leveling-bulb connected with D by thick-walled rubber tubing.

Somewhat less than a gram of piperonal is first introduced into B. The most convenient way to do this is to melt some piperonal, and draw it in through A by suction. Mercury is next poured into the bulb E, and the latter is raised until the mercury fills D and reaches the point *x*, just leaving the tube C open. Meanwhile the piperonal in B is kept melted by means of a beaker of

<sup>1</sup> This Journal, 28, 588 (1906).

warm water placed under it, and now a stream of dry hydrogen chloride is passed through the bulb, entering through A. As soon as the current is started, the warm water under B may be removed, and the gas is passed through until the crystals which at first begin to form have completely liquefied. The tubes A and C are now sealed off at the points *y* and *z*. The mixture in B is now in equilibrium with the hydrogen chloride above it at the prevailing temperature, and the whole system stands under the pressure of one atmosphere.



If, now, the bulb E be lowered, gas is evolved from the liquid in B, which begins to boil. Crystals soon appear upon its surface, and, if the quantity of piperonal has been appropriately chosen with reference to the dimensions of the apparatus, the contents of B solidify to a mass of crystals. If the bulb E be again raised, the gas is absorbed, the crystals rapidly lose their outline, and, in less than a minute, those on the surface have completely liquefied. After standing at a pressure of about an atmosphere for a few

minutes, liquefaction is complete throughout the mass. These operations can, of course, be repeated indefinitely.

The conditions here seem analogous to those which obtain between calcium oxide, carbon dioxide and calcium carbonate at a temperature in the vicinity of 800°. As the action in the present case is so rapid, and can be so readily followed by the eye, it is suggested that the experiments just described might well find use in demonstrating to students this particular application of the "phase rule."

A rough measurement of the difference in level of the mercury in bulbs D and E, when both solid and liquid are present in B, shows that the dissociation pressure of the addition product is somewhere in the vicinity of 500 mm. This is but a rough approximation. An accurate measurement has not yet been attempted, as in the experiments hitherto made I could not be certain that the hydrogen chloride was free from air. Another form of apparatus has been designed to meet this difficulty, and when the work is resumed in the autumn, more accurate measurements will be made. The question whether the addition-product is a chemical compound or a solution will then be taken up, and the investigation extended to the action of hydrogen bromide and iodide as well as other compounds upon piperalon.

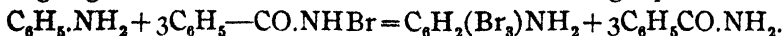
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.  
June 5, 1906.

## BENZOYL-*p*-BROMPHENYLUREA: A BY-PRODUCT IN THE PREPARATION OF BENZBROMAMIDE.

BY F. J. MOORE AND A. M. CEDERHOLM.

Received June 7, 1906.

IN 1882, Hofmann,<sup>1</sup> while carrying on his celebrated investigation of the action of bromine and alkali upon amides, discovered acetbromamide. At the same time he made the observation that this substance reacts both with aniline and with phenol to form tribromaniline and tribromphenol respectively—acetamide being regenerated in accordance with the following equation.



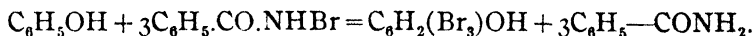
The chemical behavior of acetbromamide and analogous compounds has since been investigated by Seliwanow<sup>2</sup> and others.

<sup>1</sup> Ber. 15, 410 (1882).

<sup>2</sup> Ibid. 26, 424 (1893).

but the use of benzbromamide as a brominating agent seems not to have been adequately studied. An extended investigation of the subject is now being carried on in this laboratory. The results will be communicated later by one of us in connection with another collaborator. It is sufficient to say here that the products are not infrequently different from those obtained when bromine is employed.

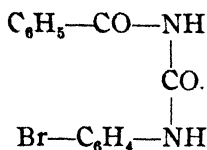
The occasion of the present investigation was an observation made while studying the action of benzbromamide upon phenol. If these substances are allowed to react in ethereal solution, the following apparent metathesis occurs, fully analogous to that observed by Hofmann.



Mixed with the tribromphenol and the benzamide, however, there appeared another substance whose presence was, at first, not so easy to explain.

*Properties of the By-product.*—This substance is a white solid, insoluble in hot and cold water, and in cold dilute alkali, but soluble in cold concentrated sulphuric acid. It is insoluble in ether, but when boiled with large quantities of alcohol, benzene, or chloroform, it dissolves, and crystallizes from each of these solvents in extremely fine silky needles. It is somewhat more soluble in glacial acetic acid, and the crystals obtained from this solvent are a little more compact. When heated in a melting-point tube of the ordinary form, the substance decomposes in the vicinity of  $227^\circ$ , with the formation of a reddish brown sublimate. If the melting-point tube be sealed off at the top before the determination is made, the substance melts quite sharply at  $230^\circ$ , and decomposes  $2^\circ$  higher. These phenomena are very characteristic. The substance contains both nitrogen and bromine. It was at first supposed that it might be a product of the action of benzbromamide upon phenol, but it soon became evident that the new substance existed as an impurity in the benzbromamide employed. From the latter it is easy to separate on account of its insolubility in cold dilute sodium hydroxide. When the impure benzbromamide is washed with this reagent, a white residue is obtained. This contains the by-product together with some benzamide. The latter is readily removed by treatment with boiling water, which dissolves the benzamide.

**Constitution.**—The investigation had reached this point when our attention was called to a paper by Stieglitz and Earle<sup>1</sup> who prepared benzoyl-*p*-chlorphenylurea by the action of phenyl isocyanate upon benzchloramide, among other methods. The properties of the compound we were studying led us to suspect that it was the analogous bromine compound—benzoyl-*p*-bromphenylurea,



This view was supported by the following analysis:

	Calculated for C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> Br. Molecular weight, 319.1.	Found.	
		I	II.
C.....	52.65	52.73	.....
H.....	3.47	3.50	.....
O.....	10.02	.....	.....
N.....	8.80	9.21	.....
Br.....	25.06	25.08	24.98

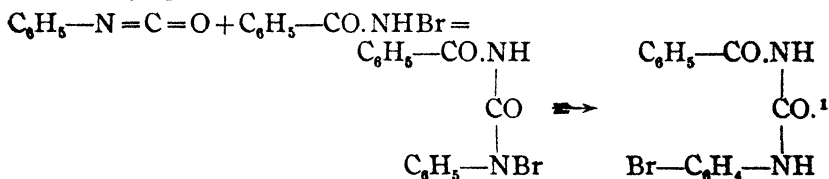
**Syntheses.**—As no description of a benzoylbromphenylurea was found in the literature, we were under the necessity of proving the constitution of the substance by synthetic methods. This was accomplished by means of reactions for the most part similar to those employed by Stieglitz and Earle in their study of the chlorine compound. One of these reactions, that of benzoyl chloride upon *p*-chlorphenylurea, was not available, as Pinnow<sup>2</sup> has studied the action of benzoyl chloride upon *p*-bromphenylurea, and found that it proceeds in a different sense, yielding benzonitrile and benzoyl-*p*-bromanilide. As the preparation of *p*-bromphenylurea itself offers some difficulties, it did not seem worth while to repeat this work on the chance of there being another product which Pinnow might have overlooked. This seemed all the more unnecessary as we were able to prepare the compound in four other ways: (1) by the action of phenyl isocyanate upon benzbromamide in benzene solution; (2) by the action of *p*-bromphenyl isocyanate upon benzbromamide in alkaline solution; (3) by the action of *p*-bromphenyl isocyanate upon benzamide when these substances are heated together; (4)

<sup>1</sup> Am. Ch. J. 30, 412 (1903).

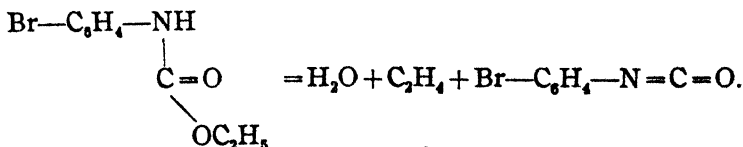
<sup>2</sup> Ber. 24, 4172 (1891).

by the action of benzbromamide upon benzoylphenylurea in benzene solution. These syntheses leave no room for doubt that the compound has the constitution already indicated.

(1) *Preparation from Phenyl Isocyanate and Benzbromamide.*—For this experiment a specially prepared and purified sample of benzbromamide was employed which was completely soluble in cold dilute sodium hydroxide, and hence could have contained no appreciable quantity of the by-product under consideration. This material was used in all subsequent synthetic experiments where benzbromamide was required. Two grams of the pure benzbromamide were heated with 1.5 grams phenyl isocyanate and 5 cc. benzene on the water-bath. At 90° all went into solution, the mixture becoming deep red in color. Soon after, a bulky white precipitate appeared, and the supernatant liquid became nearly colorless. The precipitate was filtered off, washed with alcohol, dried and recrystallized from chloroform. The crystals thus obtained melted at 227° with decomposition, and when mixed with some of the by-product obtained from the impure benzbromamide, did not depress its melting-point. The yield was nearly quantitative. The reaction is as follows:



(2) *Preparation from *p*-Bromphenylurea and Benzbromamide.*—Some difficulty was experienced in preparing the *p*-bromphenyl isocyanate for use in this and the following synthesis. At first we followed the directions of Dennstedt<sup>2</sup> who treated *p*-bromphenyl urethane with phosphorus pentoxide in accordance with the following reaction:



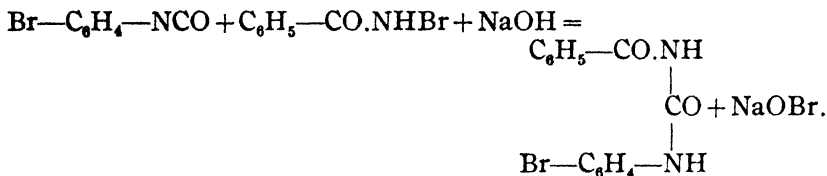
Dennstedt states that the product can be distilled off from the

<sup>1</sup> The wandering of the halogen atom has been discussed by Stieglitz and Earle.

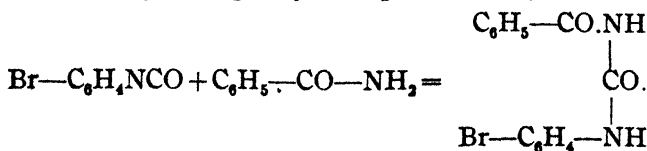
<sup>2</sup> Ber. 13, 228 (1880).

reaction mixture. In our experiments decomposition always sets in when distillation was attempted. The conditions were varied, but with no better result, and extensive decomposition was observed even when the heating was done in a bath, and the distillation conducted in vacuum. A little of the isocyanate sought could usually be identified in the distillate, but the quantity was utterly insufficient for use in further work. Attempts to distil were therefore abandoned, and the reaction mixture extracted with ligroin instead. In this way a yield of about 30 per cent. was obtained.

Four-tenths gram of the isocyanate was intimately mixed with one molecule of pure benzbromamide, and one molecule of sodium hydroxide added in the form of a 10 per cent. solution. The mixture was thoroughly shaken for twenty minutes, and then filtered. The precipitate was washed with water and then with cold alcohol. Finally it was recrystallized from hot alcohol. A melting-point comparison made as in previous cases, showed that this substance was identical with the by-product studied.

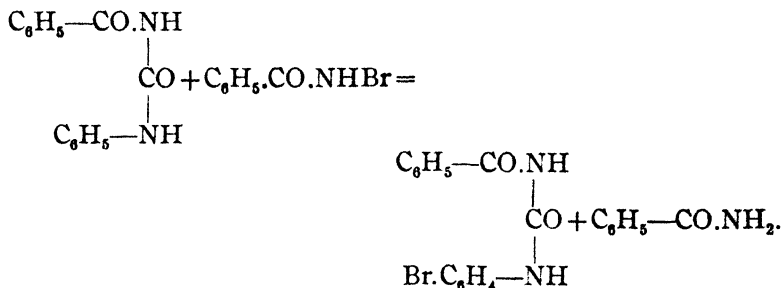


(3) *Preparation from p-Bromphenyl Isocyanate and Benzamide.*—Two-tenths gram of the isocyanate (one molecule) was intimately mixed with benzamide (one molecule) and the mixture heated in an oil-bath at 175°—thermometer in bath. An odor suggestive of bitter almonds was noticed during the heating. The dark colored reaction product was treated with hot water to dissolve benzamide, and the residue washed first with alcohol, and then with chloroform, and finally crystallized from the latter solvent. The yield was small, but the product could be identified with the benzoyl-*p*-bromphenylurea produced by other methods.



(4) *Benzoylphenyl from Benzoylphenylurea and Benzbromamide.*—Benzoylphenylurea was prepared according to the method of

Kühn<sup>1</sup> by the action of phenyl isocyanate upon benzamide. The preparation presents no difficulties. 0.25 gram of the product was heated with 0.21 gram benzbromamide in benzene solution for about twenty minutes. On cooling, a bulky white precipitate appeared. This was washed with boiling water and finally recrystallized from chloroform. The usual melting-point tests showed it to be benzoyl-*p*-bromphenylurea which must have been formed by the following reaction:



#### HOW THE BY-PRODUCT IS FORMED.

*Preparation of the Benzbromamide.*—To three molecules of sodium hydroxide in 33 per cent. solution was added two atoms of bromine with constant shaking, the flask being surrounded by ice water, and pieces of ice also being added from time to time to the reaction mixture. As soon as all the bromine had been dissolved, one molecule of finely ground benzamide was added with the same precautions. Some of the benzamide usually remained undissolved. This was removed by rapid filtration with the aid of suction, broken ice being placed in the filter bottle to keep the filtrate cold. To this filtrate, dilute, ice-cold acetic acid was added as long as a precipitate formed. At this point a red color was observed and the solution smelled strongly of bromine. This must have come from the reaction of the acid upon some hypobromite or bromate present in the solution along with the excess of sodium bromide. The precipitate was then filtered off, freed as much as possible from the mother-liquor by suction, and dried on porous plates. It was usually left spread out on these over night, and then crystallized from boiling benzene. Two crystallizations were usually necessary to secure a colorless product. The crystals thus obtained were flaky in structure, and the forms were not well marked.

<sup>1</sup> Ber. 17, 2880 (1884).



It will be observed that the method just described closely follows the directions of Hoogewerff and Van Dorp<sup>1</sup> also recommended by Hantzsch.<sup>2</sup> It differs in the use of sodium instead of potassium hydroxide and also in the use of an alkali solution which was more concentrated at the beginning of the reaction. As ice was added freely while the reaction progressed, the solution was probably as dilute at the end of the reaction as in the experiments of Hoogewerff and Van Dorp.

In our first experiments, about 50 grams of benzamide were used for each preparation. Later, when it became necessary to prepare especially pure material, only 10 grams were used, and about the same routine followed, except that additional pains were taken to perform all operations as slowly and at as low a temperature as possible. The substance prepared in this way crystallized in lustrous plates and was entirely soluble in cold dilute sodium hydroxide.

The impure product first described showed a tendency to grow reddish in color on standing, and emitted an odor resembling that of bromine. This led us to think that the formation of the brominated urea might be traced to a spontaneous decomposition of the benzbromamide, either while drying in contact with the dilute acetic acid or in the benzene solution during the process of crystallization, or, finally, by standing in the bottle. Various experiments were made to test these points, the details of which need not be given here. The crystalline impure benzbromamide was allowed to stand at various temperatures, both dry and in the presence of dilute acetic acid; it was also boiled with a return condenser for varying lengths of time both in benzene and in toluene solution. In none of these cases was it apparent that the amount of benzoyl-*p*-bromphenylurea in the product had perceptibly increased. The cause of its formation had, therefore, to be looked for at some earlier stage.

#### CONCLUSION.

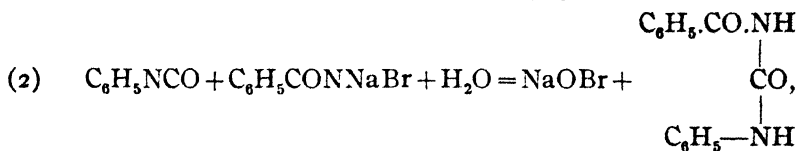
We finally concluded that the key to the solution of this problem was to be found in an observation of Van Dam and Aberson.<sup>3</sup> These investigators found that a dilute solution of the potassium salt of benzbromamide decomposes with the formation of benzoyl-

<sup>1</sup> *Rec. trav. chim.* 8, 188 (1889).

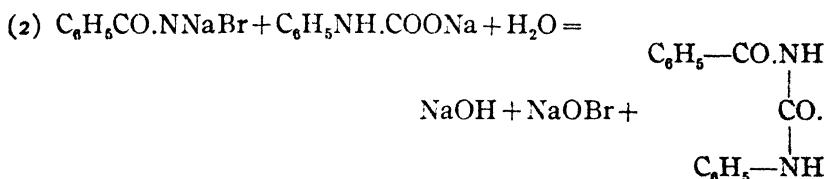
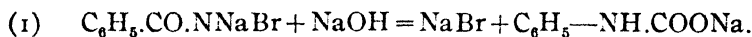
<sup>2</sup> *Ann.* 296, 86 (1897).

<sup>3</sup> *Rec. trav. chim.* 19, 318 (1900).

phenylurea, and further that the reaction proceeds more rapidly in this sense, the more nearly neutral the solution. This behavior can be represented by the following equations, assuming the presence of some phenyl isocyanate at this point, (this would be in harmony with the views of most students of Hofmann's reaction):



or if with E. Mohr,<sup>1</sup> sodium phenylcarbamate is assumed as an intermediate product,



In the preparation of benzbromamide, when the acetic acid is added, the neutral solution favorable for these reactions is produced, and the precipitate consists of a mixture of benzbromamide and benzoylphenylurea. When this mixture is crystallized from benzene, the latter is brominated by the former in accordance with the reactions described in the fourth synthesis mentioned above. In fact this synthesis was originally carried out to test this very point.

Another possibility has to be considered. It has been already noted that when the acetic acid is added, some bromine seems to be liberated. This might effect the bromination. We are inclined to reject this hypothesis, partly because the last synthesis just alluded to has shown that the benzbromamide can accomplish this result, partly because Van Dam and Aberson and other investigators have only observed the non-brominated product, and partly because where the brominated urea has been met with, it has been accompanied by benzamide. The presence of the latter can be most easily accounted for on the assumption that

<sup>1</sup> J. pr. Chem. [2] 73, 177 (1906).

benzbromamide is the brominating agent. Furthermore, it is not easy to see why a substance as insoluble as benzoylphenylurea should be much affected by dilute bromine water.

The improvement in the quality of benzbromamide when only small quantities were prepared, is doubtless to be explained by the fact that, under these circumstances, it is easier to maintain a low temperature throughout, less of the benzbromamide being decomposed to form isocyanate or carbamate.

#### SUMMARY.

When benzbromamide is prepared by the method of Hoogewerff and Van Dorp, it is liable to contain benzoyl-*p*-bromphenylurea. The amount of this substance may sometimes exceed 10 per cent.

Benzoyl-*p*-bromphenylurea is a bulky, colorless, crystalline solid. It melts in a closed tube at 230° and decomposes at 232°. It is soluble with difficulty in most of the ordinary organic solvents.

The constitution assigned to this compound is most conclusively proved by its synthesis from *p*-bromphenyl isocyanate and benzamide, but it is also consistent with its preparation by three other syntheses, with the analysis, and with its whole behavior.

The formation of the benzoyl-*p*-bromphenylurea in the preparation of benzbromamide is to be accounted for as the result of the bromination of the benzoylphenylurea first formed. This bromination is probably effected by the benzbromamide itself.

The authors perform a pleasant duty in acknowledging their indebtedness to Dr. Richard B. Earle, instructor in organic chemistry at the institute, for many helpful suggestions.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.  
June 5, 1906.

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### NOTES ON SOME OF THE CONIFER OILS.

BY R. E. HANSON AND E. N. BABCOCK.

Received June 20, 1906.

AN apparent want of conformity in the present literature on some of the conifer oils has led us to investigate several of them, and we hereby embody the results of our work.

Our investigation has been confined to the following oils:

(A) Black spruce (*Picea Mariana*) leaves.

Hemlock (*Tsuga Canadensis*) leaves.

(B) American larch (*Larix Americana*) leaves.

White spruce (*Picea Canadensis*) leaves.

White spruce (*Picea Canadensis*) cones.

Red spruce (*Picea rubens*) leaves.

Red spruce (*Picea rubens*) cones.

Pitch pine (*Pinus rigida*) leaves.

Red pine (*Pinus resinosa*).

Juniper (*Juniperus communis*) leaves.

All of the oils in division marked B are, to the best of our knowledge, distilled and herein described for the first time.

Throughout the work we have carefully identified all materials from which the oils have been distilled and have personally superintended the distillation to insure the purity of the oils.

(1) *Oil of Black Spruce* contains 48.85 per cent. bornyl acetate (Kremers), sp. gr. 0.922 at 20° (Gildmeister and Hoffmann). An oil distilled by us was obtained in a yield of 0.57 per cent. and had a sp. gr. of 0.9274 at 19°. Change in the specific gravity of its fresh oil for 1°, 0.0010; for oil which has stood for some time 0.0014.

(2) *Oil of Hemlock* contains 51.5-52 per cent. of bornyl acetate—sp. gr. 0.9288 at 20° (Hunkel). According to Gildmeister and Hoffmann, it contains 36 per cent. bornyl acetate, sp. gr. 0.907-0.913. An oil distilled by us from leaves and twigs of a large tree was obtained in a yield of 0.4 per cent., sp. gr. 0.9238 at 15°. A second distillation from the leaves and twigs of a small tree gave a yield of 0.46 per cent., sp. gr. 0.9273 at 15°. Change in its specific gravity of the fresh oil for 1°, 0.0010.

(3) *Oil Picea Canadensis* (Cat Spruce) has apparently not been investigated, although we have reason to believe it is often confused with black spruce in the distillation of the latter. We obtained this oil in a yield of 0.103 per cent., sp. gr. 0.9216 at 15°. Change in the specific gravity for 1°, 0.0012. It contains 25.7 per cent. of ester, calculated as bornyl acetate, which is a low ester content in comparison with the other spruce oils. The odor of this oil is distinctly different from that of black spruce and hemlock oils, suggesting limonene or dipentene. We are at

present engaged upon the identification of the terpenes present in this oil.

(4) *Oil Picea Rubens* (Red Spruce).—This oil is remarkable for its high specific gravity and high percentage of ester. The distillation gave a yield of 0.204 per cent., sp. gr. 0.9539 at 16°. Change in the specific gravity for 1°, 0.0014. This oil contains 66.2 per cent. of bornyl acetate and 7.76 per cent. of free borneol. On saponification, large quantities of crystals having a distinct odor of borneol separated out. After recrystallizing several times from petroleum ether the borneol appeared as white, shining, hexagonal plates melting, but not sharply, in the neighborhood of 200°. Lack of sufficient quantity of oil prevented us from obtaining crystals with the melting-point of pure borneol, 206°, or from forming derivatives and thus making a positive identification.

The oil itself had a very agreeable odor, strongly suggestive of borneol acetate.

(5) *Oil Larix Americana*.—This oil, distilled from the leaves and twigs was obtained in a yield of 0.149 per cent., sp. gr. 0.8816 at 15°, ester content 15.1 per cent., calculated as bornyl acetate.

Fractional distillation gave the following results:

155°–170°	=	20	per cent.
170°–180°	=	38.4	" "
180°–190°	=	11.2	" "
190°–200°	=	9.2	" "
200°–240°	=	14.8	" "
Residue	=	6.4	" "
<hr/>			
Total	=	100	" "

The fraction 170–180° was redistilled when 62 per cent. boiled below 171°; 20.5 per cent. boiled at 171–181°. The remainder was the residue, boiling above 181°.

The fractions distilling below 171° were combined. The specific gravity of these combined fractions was 0.8578 at 15°. Two more redistillations of the fractions below 171° yielded a fraction boiling at 155–162°. From this last fraction we were enabled to obtain a nitrosochloride which melted sharply at 108°. This is the melting-point of pure pinene nitrosochloride.<sup>1</sup> Owing to paucity of material, we did not attempt to form the nitrol-

<sup>1</sup> Van Romburgh: See Schimmel's Report, April, 1901.

benzylamine compound, which would have established still more firmly the presence of pinene.

According to our investigations, 15.1 per cent. of this oil is ester (calculated as bornyl acetate) and the remainder is largely pinene.

(6) *Picea Rubens* (Cones).—This oil was obtained in a yield of 0.38 per cent., sp. gr. 0.8600 at 15°, with a golden yellow color and a fir-balsam-like odor.

(7) *Oil of Picea Canadensis* (Cones).—This oil was obtained in a yield of 0.25 per cent., sp. gr. 0.899 at 15°. It was of a yellow color and a pronounced limonene-like odor. These constants were taken some time after the oil had been distilled, and the high specific gravity may be due to a subsequent thickening.

(8) *Oil Pinus Rigida*.—The yield of this oil was extremely small. From 12 kg. of leaves and twigs we obtained only 0.2 cc. Oil was yellow in color and had an extremely pungent odor.

(9) *Oil Pinus Resinosa*.—The yield of this oil was also very small, about 0.001 per cent. The color of the oil was a brownish red. Its odor was very pungent and disagreeable.

(10) *Oil Juniperus Communis*.—Leaves and twigs, devoid of berries, were used in the distillation of this oil. The oil was obtained in a yield of 0.18 per cent. in one distillation, while a second distillation of material from other ground gave nearly the same yield, 0.15 per cent. These distillations were carried on in the spring about the first of May. Specific gravity of the oil was 0.8531 at 20°. Oil was of a light yellow color and characteristic juniper odor.

(11) *Oil Juniperus Virginiana* (Leaves).—An oil distilled by us had a slightly higher density than is generally given. Sp. gr. 0.900 at 16°.

Owing to lack of sufficient quantities of the oils we have been unable to carry these investigations further as yet. Arrangements are being made, however, for the distillation of larger quantities of several of them as well as other new oils of the same species. We hope to be able to present more complete results in the near future.

## THE DETECTION OF METHYL ALCOHOL.

BY HEYWOOD SCUDDER AND ROBERT B. RIGGS.

Received June 23, 1906.

LEACH and Lythgoe<sup>1</sup> recommend as a confirmatory test for the detection of methyl alcohol, oxidation of the solution by a hot copper spiral and testing for formaldehyde by heating with milk and hydrochloric acid containing ferric chloride.

We have tried this test on 10 per cent. aqueous solutions of ethyl alcohol, acetic acid and acetone, and in each case there developed a violet color indistinguishable from that given by pure methyl alcohol. After oxidation the solutions were filtered before adding the milk and acid. The color obtained depends somewhat on the conditions of the test. Leach directs the use of a few drops of the oxidized solution.

In the case of acetone, if the whole of the oxidized solution was used, a distinct violet color appeared momentarily during the heating, changing to a brownish yellow. If only a few drops of the oxidized solution were used the violet color was deep and persistent. But on adding to this the rest of the oxidized solution (which contained a good deal of unaltered acetone) and heating, the violet color disappeared, changing to brownish yellow. In this case the excess of the acetone gave a color that obliterated the color due to formaldehyde.

In the case of ethyl alcohol there is a difference in the depth of the violet color between tests made with a few drops and with the whole of the oxidized solution, but the violet always persists.

Acetic acid showed no difference in color whether a few drops or the whole solution was used.

Oxalic acid gave a brown with a faint violet tinge, when a few drops of the oxidized solution were tested, but excess of the oxidized solution destroyed this violet, leaving only the brown. The violet tinge was sufficiently marked to be noticeable to one unaccustomed to the test.

A blank test of the milk used, showed no trace of a violet tinge under any variations of heating.

The cause of the failure of this test is its delicacy in detecting formaldehyde. The formation of small amounts of formaldehyde in the oxidation of many organic compounds, especially

<sup>1</sup> This Journal, 27, 965 (1905).

when the oxidant is heated copper or platinum, is well-known,<sup>1</sup> and warnings have been given of the caution necessary in applying any test for methyl alcohol that depends on a very delicate test for formaldehyde.

In the case of the compounds tested, the violet color came from formaldehyde. If a sufficient amount of some other compound reacting with milk and acid was present (as in the case of acetone and oxalic acid) the violet color became changed or obliterated, otherwise it persisted.

In its present condition this test can not be depended on as a general one for the detection of methyl alcohol in mixtures.

*The Sanglé-Ferrière Cumiasse Test*<sup>2</sup> we have modified so that it can be performed more simply. This modification shows 2 to 3 per cent. of methyl alcohol in ethyl. To 10 cc. of the aqueous solution to be tested are added 0.5 cc. of concentrated sulphuric acid and 5.0 cc. of a saturated solution of potassium permanganate. The temperature should be kept at 20°–25°. At the end of two minutes enough sulphurous acid is added to give a colorless solution (an excess is not harmful). The solution is boiled till it does not smell of sulphur dioxide nor of acetaldehyde, then the resorcinol test for formaldehyde is applied. If no flocks appear but a pink ring is present, they can often be developed by standing for one to two hours, then heating the upper layer just to boiling. The ring first formed is usually sufficiently characteristic to show methyl alcohol and in case of doubt a blank test with ethyl alcohol can be made, but the flocks give positive evidence and no blank is required.

The use of sulphurous acid to reduce any excess of the permanganate and to dissolve the hydroxide avoids the troublesome precipitation by tannic acid and sodium carbonate with subsequent filtration.

Variations in the temperature below 18° are harmful from the reduced speed of the reaction, above 30°, from loss of formaldehyde. Great excess of acid is harmful. Less acetaldehyde seems to be formed from ethyl alcohol in this oxidation than in the oxidation with a hot copper spiral.

*Formation of Flocks in the Resorcinol Test for Formaldehyde.*—

<sup>1</sup> Mulliken, Brown, French: Am. Ch. J. 25, 115 (1901); Scudder: This Journal, 27, 894 (1905).

<sup>2</sup> Ann. chim. anal. appl. 8, 82 (1903).



If to the solution to be tested are added an equal volume of concentrated hydrochloric acid and two drops of a 0.5 per cent. solution of resorcinol and the whole is boiled one or two minutes, characteristic flocks will appear, if sufficient formaldehyde is present.

The advantage of using hydrochloric acid instead of sulphuric acid is that no darkening of color from overheating or charring is possible. The disadvantage is that the delicacy of the test is lessened. It is not possible to get flocks in mixtures of methyl and ethyl alcohols when less than 5 per cent. methyl alcohol is present. The boiling, of course, prevents any formation of a contact ring. But when sulphuric acid is used, the color of the flocks is often destroyed by too rapid shaking, with consequent overheating, especially when only a small amount of formaldehyde is present.

TRINITY COLLEGE, HARTFORD.

## A METHOD FOR THE DETERMINATION OF LEAD NUMBER IN MAPLE SYRUP AND MAPLE SUGAR.

BY A. L. WINTON AND J. LEHN KREIDER.

Received July 5, 1906.

THE copious precipitate formed in maple products by basic lead acetate furnishes a means not only of clearing the solution for polarization but also of detecting the admixture of refined cane-sugar. Jones<sup>1</sup> and also Hortvet,<sup>2</sup> working independently of each other, have devised methods for measuring the bulk of this precipitate after separation with the aid of a centrifuge. The method devised by Jones was especially designed to test the products delivered by farmers to wholesalers, while Hortvet's method was devised with reference to the official inspection of the commercial products. Both serve well the purpose for which they were intended; they are easily carried out and give comparative results of great value. These results, however, can hardly be accepted as fixed constants, since the precipitate varies not only in composition but its volume is also dependent on the speed of the centrifuge and other details of manipulation.

Although volumetric methods of a similar nature are successfully employed for the determination of the gravimetric per-

<sup>1</sup> *Vt. Agr. Expt. Sta. Rep.* 17, 454 (1904).

<sup>2</sup> *This Journal*, 26, 1532 (1904).

centages of fat (*e. g.*, Babcock method) and essential oil (*e. g.*, Mitchell's method for determining the oil in lemon extract), it is impracticable to convert the volume of a solid precipitate into percentages even when the precipitate is of definite composition and the task is obviously impossible when it is a variable mixture.

It also appears to us impracticable to weigh this precipitate, owing to difficulties in filtering, washing and drying.

The plan which seems to best serve the purpose is not to determine the total percentage of the precipitate but the amount of lead contained in it. This lead could be determined in the precipitate itself but this would involve careful washing and separation from the organic matter, both of which are laborious operations.<sup>1</sup> We have employed an indirect method, using a definite volume of standard lead subacetate and determining the lead remaining in the solution after precipitation. In order to still further reduce the labor of the operation the solution of the material after precipitation is made up to a definite volume, filtered through a dry paper, and the lead determined as sulphate in an aliquot portion of the filtrate.

The method adopted by us is in detail as follows:

*Description of the Method.*<sup>2</sup>—Weigh 25 grams of the material (or 26.048 grams if it is desired to determine sugars polariscopically in the same portion) into a 100 cc. flask. Add 25 cc. of standard lead subacetate solution, fill to the mark, shake, allow to stand at least one hour, and filter. From the clear filtrate pipette off 10 cc., dilute to 50 cc., add a moderate excess of sulphuric acid and 100 cc. of 95 per cent. alcohol. Let stand over night, filter on a Gooch crucible, wash with 95 per cent. alcohol, dry at a moderate heat, ignite at low redness for three minutes, taking care to avoid the reducing cone of the flame, and weigh. Calculate the amount of lead in the precipitate (factor 0.6829), subtract this from the amount in 2.5 cc. of the standard solution, and divide the remainder by 2.5 thus obtaining the "*Lead Number*."

The standard lead subacetate is prepared as follows:<sup>3</sup> Boil for half an hour 430 grams of normal lead acetate and 130 grams of

<sup>1</sup> Since this paper was read at the Ithaca meeting of the Society (June 28, 1906) Prof. Albert P. Sy has published a paper describing a method of determining the lead directly in the precipitate (J. Franklin Inst. July, 1906, p. 71).

<sup>2</sup> Devised by A. L. W.

<sup>3</sup> U. S. Dept. Agr., Div. Chem. Bull. 65, p. 84.

litharge with 1000 cc. water. Cool the mixture, allow to settle, and dilute the supernatant liquid to 1.25 specific gravity. To a measured amount of this solution add four volumes of water and filter if not perfectly clear.

The standard of the solution is determined in 25 cc. by the lead sulphate method as above described. On standing it deposits a slight precipitate, but our tests show that the strength is not appreciably affected in a month or six weeks.

Given sufficient Gooch crucibles about 24 determinations of the lead number can be made in eight hours distributed through two days.

*Test of Different Standard Solutions, Time Required for Precipitation.*—As basic lead acetate solution varies somewhat in composition dependent on impurities in the chemicals used and irregularities in the process of preparation, it is important to ascertain whether these variations affect the precipitating power. It is equally important to determine the time required for complete precipitation. To decide these points comparative analyses were made on three samples of pure and three of adulterated maple syrup, using three solutions prepared from different lots of chemicals and allowing to stand after the precipitation one and eighteen hours. Solutions A and B were prepared from different lots of commercial lead acetate and litharge, solution C from the chemically pure materials.

The results are given in Table I.

TABLE I.—COMPARISON OF RESULTS ON LEAD NUMBER IN PURE AND ADULTERATED MAPLE SYRUPS, USING DIFFERENT STANDARD SOLUTIONS OF LEAD SUBACETATE AND STANDING ONE AND EIGHTEEN HOURS AFTER PRECIPITATION.

	Pure.						Adulterated.					
	No. 15988.		No. 15989		No. 16037.		No. 15967		No. 15970.		No. 15993.	
	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.
Solution A	1.88	2.04	1.52	1.62	1.63	1.84	0.00	0.00	0.16	0.13	0.46	0.44
" B	2.03	2.12	1.60	1.64	1.71	1.93	0.02	0.02	0.13	0.18	0.31	.....
" C	2.14	2.05	1.70	1.82	1.94	1.93	0.00	0.04	0.23	0.31	0.34	.....

From these results it appears that no fear need be apprehended as to variations in the precipitating power of the standard solution; also that standing one hour gives virtually the same results as standing eighteen hours.

It should here be stated that in the case of all the pure samples,

which we have examined, the solution filtered from the lead precipitate after standing one hour remained clear on further standing. The same is also true of all the adulterated samples but one. The latter, No. 16036 Table III, gave a lead number of 0.13 on standing one hour and of 0.42 on standing eighteen hours. Since one hour was found sufficient for all pure samples it is reasonable to assume that the extra amount obtained on long standing from this adulterated sample is due to some foreign constituent and may be justly disregarded.

*Results on Authenticated Samples.*—The following results, obtained on samples of known purity kindly supplied by Mr. C.

TABLE II.—RESULTS ON LEAD NUMBER AND TOTAL SOLIDS IN AUTHENTICATED SAMPLES OF MAPLE SYRUP AND MAPLE SUGAR.

No.		Total solids	Lead number.
1	Maple syrup, excellent quality, composite sample.....	64.16	{ 1.54 1.54
2	" " " " " " .....	64.07	{ 1.39 1.38
3	" " " " " " (Ohio) .....	68.49	{ 1.21 1.19
4	" " " " (made in 1893).....	64.53	{ 1.49 1.47
5	" " good quality, composite sample.....	68.28	{ 1.66 1.66
6	" " medium quality, " " ....	66.21	{ 1.57 1.57
7	" " " " " " .....	64.86	{ 1.40 1.40
8	" " poor quality.....	65.59	{ 1.77 1.77
9	Maple sugar (American), good quality.....	99.24	{ 2.07 2.10
10	" " " " " " .....	99.20	{ 2.37 2.38
11	" " " medium quality.....	98.99	{ 2.30 2.29
12	" " " " " " .....	98.43	{ 2.47 2.48
13	" " " composite sample.....	99.28	{ 2.18 2.17
14	" " (Canadian), good quality.....	94.99	{ 2.35 2.36
15	" " " " " " .....	94.63	{ 1.83 1.84

H. Jones, chemist of the Vermont Station, give a general idea of the variation in the lead number in the normal product although these results should be supplemented later by others on samples from other localities before the range in the lead number can be finally decided.

*Results on Samples Found on the Market.*—We have recently made analyses of 38 brands of maple syrups found on sale in Connecticut which show that only three were the genuine products, the remainder being mixtures consisting largely of refined cane-sugar. The determinations made include not only lead number but also, for comparison, total solids, cane-sugar (by Clerget's formula), Hortvet number (volume of the lead precipitate), and total ash. The lead number in the samples classed as pure ranged from 1.61 to 2.03, while in the adulterated samples it ranged from 0.02 to 0.92. In Table III are given such of these analyses as serve to show the range in composition of the samples.

It is a remarkable fact that every result in this table, except those for total solids and sucrose, furnishes decided evidence of purity or adulteration. Even the percentages of total solids and sucrose are useful, since the difference between the two is usually greater in the case of the pure syrups.

For a consideration of other methods of value in detecting adulteration the reader is referred to the exhaustive papers of Hortvet<sup>1</sup> and Jones.<sup>2</sup>

It has been suggested that the lead number of adulterated maple products can be so increased by the addition of various substances as to equal that of the genuine products. That this is true can not be denied, but it is also true that the results for ash and other constituents of these products as well as many of the constants of other food products can be rendered valueless as a means of detecting adulteration by skilful manipulation. The task, however, becomes more difficult with the introduction of new constants, especially when these are based on different principles.

The determination of ash and its characters and of lead number will usually suffice for the detection of the adulterants now in common use.

<sup>1</sup> Loc. cit.

<sup>2</sup> Loc. cit.; Vt. Agr. Expt. Sta. Rep. 18, 315 (1905).

TABLE III.—ANALYSES OF MAPLE SYRUP FOUND ON THE MARKET.

Serial number.		Total solids. Per cent.	Sucrose by Clerget's formula. Per cent.	Hortvet number. <sup>1</sup>	Lead number.	Total ash. Per cent.
15988	Pure.....	66.98	62.4	1.00	2.03	0.75
15989	Pure.....	67.29	61.6	0.69	1.61	0.60
16037	Pure.....	66.40	59.5	1.24	1.89	0.54
15929	Adulterated <sup>2</sup> .	66.40	65.4	0.15	0.66	0.14
15932	Adulterated..	66.90	65.4	0.15	0.48	0.16
15945	Adulterated..	65.81	.....	0.22	0.87	0.23
15948	Adulterated..	67.61	67.8	0.07	0.52	0.04
15961	Adulterated..	63.18	.....	0.07	0.10	0.02
15967	Adulterated..	68.62	67.6	0.07	0.02	0.04
15970	Adulterated..	66.58	65.2	0.11	0.19	0.19
15971	Adulterated..	69.49	68.4	0.11	0.43	0.07
15982	Adulterated..	64.53	61.9	0.15	0.17	0.17
16005	Adulterated..	65.57	.. ..	0.15	0.12	0.04
16006	Adulterated..	66.13	65.2	0.11	0.66	0.08
16035	Adulterated..	65.33	60.0	0.12	0.92	0.14

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## ON THE DETERMINATION OF CARBON DISULPHIDE AND TOTAL SULPHUR IN COMMERCIAL BENZENE.

BY EDWARD S. JOHNSON

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CRUDE, unwashed benzene, or the so-called "benzol light oil," contains as certainly identified sulphur compounds, hydrogen sulphide, carbon disulphide, thiophene and its homologues. There are doubtless others among the unsaturated compounds which become eliminated in the first stage of benzene purification, the washing with concentrated sulphuric acid. There is left after this treatment in the lower-boiling fractions derived from the washed benzene, as a main impurity carrying sulphur, carbon disulphide. Thiophene, as well-known, represents the chief of other sulphur bodies present.

### I. THE DETERMINATION OF CARBON DISULPHIDE.

The principle underlying the method seemingly most widely practiced is that of the transformation of carbon disulphide by means of alcoholic potash into potassium xanthate, utilizing this

<sup>1</sup> Cubic centimeters of lead precipitate from 5 grams of the material.

<sup>2</sup> The adulterated samples were mixtures of maple syrup and refined cane-sugar. Some were labeled as compounds and therefore were not legally adulterated.

substance as a medium of separation for the sulphide. For the determination of the sulphide the xanthate has variously been weighed as such, converted into cuprous xanthate, and again titrated with cupric sulphate solution. Nickels<sup>1</sup> seems first to have applied the xanthate reaction to a separation of carbon disulphide from benzene. The volumetric method referred to originated with Macagno<sup>2</sup> with a view, however, of applying the process to the assaying of carbon disulphide preparations.

The method of Nickels<sup>3</sup> to determine the sulphur finally by weighing the potassium xanthate or cuprous xanthate derived from it *as such* is attended by several inaccuracies. When operating with the potassium salt it must be separated by filtration and washed with ether. The mother-liquors are merely drawn or drained off and leave a precipitate contaminated by adhering alkali not removed by the ether. It is constantly undergoing decomposition on exposure to air. The cuprous salt is more stable but cannot be brought to constant weight without decomposition even by moderate warming after water-washing. By ether treatment of the precipitate freed from the mother-liquors, a more successful drying might result. In view of the somewhat unstable character of the compound, however, the determination as copper oxide, after ignition of the precipitate, promised more satisfactory results. Much uncertainty exists apparently as to the exact composition of the so-called cuprous xanthate. If constituted as represented by the formula  $(\text{CS}.\text{OC}_2\text{H}_5\text{S})_2\text{Cu}$ , the ratio of copper oxide produced to carbon disulphide entering into the formation of the xanthate should be 1.0:0.9563. In establishing the basis of his volumetric method, Macagno made some determinations of the ratio and found 1.0:1.931 not much varying from *twice* the theoretical. Others have obtained similar results indicating approximately the relationship  $2\text{CS}_2:\text{CuO}$ . As evidently cuprous xanthate is not the compound under consideration, judging from the ratios thus discovered, and recalling the instability of the body resulting from the action of cupric sulphate on potassium xanthate, a reopening of the question as to the ratio of the copper compound obtained on ignition of the xanthate produced by a known weight of carbon dioxide seemed

<sup>1</sup> Chem. News, 43, 148.

<sup>2</sup> Ibid. 43, 138.

<sup>3</sup> Attributed to him by Allen: Comm. Organ. Anal.

justified. An investigation appeared the more desirable because of a strong probability of a variation in composition with changing conditions of formation. Experiments were, therefore, made, having in mind a process for the separation and determination of carbon disulphide contained in benzene by means of the xanthates, the method being adapted to convenient manipulation and conditions easily realized and thus maintained constant. The ratio of copper oxide, yielded by the yellow xanthate upon ignition, to the carbon disulphide from which it was derived under the given circumstances was made the subject of the experiments, an account of which follows:

*1. Determination of the Ratio of the Copper Ignition-Residue to Carbon Disulphide.*

That the ratio might be an expression of the many experimental factors in a determination of carbon disulphide in benzene, known weights of a perfectly pure sulphide were dissolved in a specially prepared benzene, the sulphide transformed into potassium xanthate, which was separated and determined, as to be described.

*The Separation of the Carbon Disulphide as Xanthate.*—As intimated above, the matter-of-course precaution was taken to apply a preparation of carbon disulphide of high purity, and the usual manipulations in the weighing and transfer of so volatile a substance without loss were employed. The weighed portions of the sulphide were added to about 75 cc. of pure benzene contained in a glass-stoppered flask of 250 cc. capacity. Besides the benzene the flask already contained for each 0.1 gram of carbon disulphide about 1 cc. of a saturated alcoholic solution of potassium hydroxide. The sulphide was then liberated from the weighing vessel and the mixture agitated fifteen to twenty minutes. The potassium xanthate formed was dissolved by addition of water, and the aqueous xanthate solution and benzene transferred to a separating funnel. The solution was drawn off and the benzene well washed. The extraction was repeated with about three-quarters of the original amount of potassium hydroxide solution, and a third time should a separation of xanthate crystals occur in a second extraction. The extracts and washings were diluted to 500 cc. and aliquot parts applied for precipitation.

*The Precipitation as Cuprous Xanthate and Determination as*



*Copper Oxide.*—The alkaline xanthate solution was acidified with acetic acid, used well diluted and in very slight excess. Immediately the cold solution was treated with copper sulphate solution (1 : 5) in distinct but not great excess. During standing for one to one and one-half hours after the precipitation, the precipitate was repeatedly stirred. It has most agreeable qualities for quantitative manipulations. Filtration and water-washing are expeditious and perfect. The filtrate passed the filter clear as did the washings, as just implied, but upon standing for some hours, for instance over night, slight further precipitation invariably took place. In the experiments under discussion, this precipitate was collected and added to the main portion. In the usual technical analysis the amount of xanthate here concerned is so small as to become negligible. This second precipitation is presumably caused by dissolving of the compound in the washings in which it is more soluble than in the liquors in which it forms.

At once after the washing the precipitate was removed to a porcelain crucible, dried and ignited. A constant weight was easily obtained. The product of the ignition, in the main copper oxide, may also contain, where large precipitates are involved, some cuprous sulphide, a consideration which evidently in nowise disturbs the ratio sought.

## 2. *The Data Obtained.*

In the table below are found the results of a number of determinations of the  $\text{CS}_2$ -CuO ratio. No pretense is here made to an exhaustive investigation of the subject. Those points only which plainly require consideration for the purpose of establishing a method of sufficient accuracy for technical application were given attention. The variation in the ratios developing under circumstances defined in the table indicate need of still more detailed limitation of conditions. The relation of the xanthate to the quantity of alcoholic potash by which it is formed, the acidity and dilution of the solution upon precipitation of the copper salt and the excess of copper sulphate are all factors which, when exactly determined and considered, would eliminate in all probability, variations in the ratios appearing under identity of those conditions thus far investigated.

THE RATIO OF COPPER OXIDE TO CARBON DISULPHIDE UNDER VARYING  
CONDITIONS OF EXPERIMENT.

No.	CS <sub>2</sub> .	Excess CuSO <sub>4</sub> .	Age of xanthate solution	Time for precipitation.	CuO.	CuO : CS <sub>2</sub> . CuO = 1.0.
3	0.06038	Slight	Fresh	0 hrs.	0.0349	1.730
4	0.06038	Moder.	"	16 "	0.0379	1.593
7	0.06038	"	2-3 das.	1 ½ "	0.0354	1.706
1	0.08534	Large	Fresh	¾ "	0.0488	1.749
2	0.08534	Moder.	"	¾ "	0.0474	1.800
5	0.08534	Slight	3 das.	1 "	0.0494	1.728
8	0.13710	Moder.	Fresh	¾ Stir.	0.0747	1.825
9	0.13710	"	2 das.	20 hrs.	0.0805	1.703
10	0.13710	Moder.	3 "	1 ½ "	0.0770	1.780

In comparison with the results of former work, a much *lower ratio* is seen to exist under the circumstances detailed. The average is 90 per cent. of the Macagno ratio.

Among the factors taken into account in the present series of experiments, those of the size of the precipitate (quantity of carbon disulphide present) and time of standing before filtration appear as of most significance. The results from the use of 0.06 gram of carbon disulphide are about 5 per cent. lower than when 0.14 gram was applied. The influence of time on the precipitation is shown by 3 and 4, and again by 9 and 10; the former instances, for the longer period, show an 8 per cent. lower ratio; the latter, one by 4 per cent. lower. As representing the results to be obtained by the method described, No. 7 for 0.06 CS<sub>2</sub>, Nos. 2 and 5 for 0.085 CS<sub>2</sub> and No. 10 for 0.14 CS<sub>2</sub> have been selected as working factors and the average as a general working factor. An extreme difference of about 4.0 per cent. exists. With a benzene containing 2 per cent. carbon disulphide, a variation of less than 0.10 per cent. would be involved by the use of the lowest and the highest factor. The average of 1.750 was adopted for general practice.

WORKING FACTOR IN RELATION TO CARBON DISULPHIDE CONCERNED IN  
ITS PRODUCTION AND THE AVERAGE FACTOR.

CS <sub>2</sub>	Working factor.	Average factor.
0.06038	1.706	1.676
0.08534	1.764	1.759
0.13710	1.780	1.773
	-----	-----
	Average, 1.750	1.736

Below are tabulated several results of carbon disulphide determinations in benzene samples, 90 and 100 per cent., by the method derived from the data secured in the above experiment.

## RESULTS OF ANALYSES BY THE METHOD DESCRIBED.

Sample No.	Determination.		Difference.
	I.	II.	
1 .....	0.809	0.765	0.044
2 .....	0.475	0.477	0.002
3 .....	0.442	0.414	0.028
4 .....	0.743	0.764	0.003

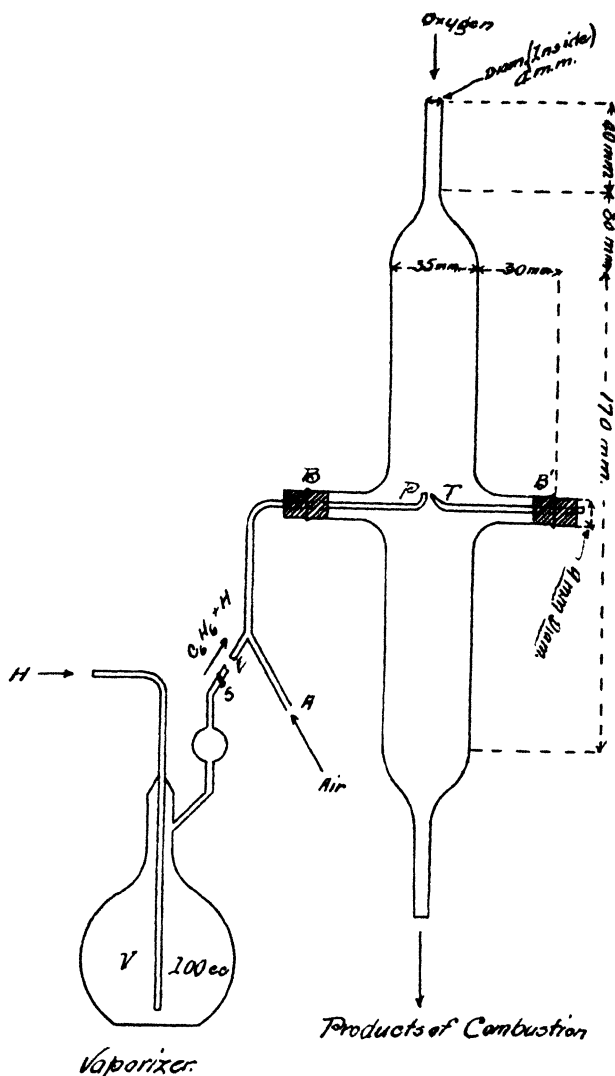
## II. DETERMINATION OF TOTAL SULPHUR IN BENZENES.

The determination of total sulphur in benzene by the usual method of Carius for organic compounds is wholly impracticable. Acting in part on suggestions extant, as a result of the work of the older and more recent investigations in this field, it was sought to accomplish the purpose by vaporizing the hydrocarbon and combustion of the gas-mixture in an atmosphere of oxygen. The products of the combustion were passed into a suitable absorption medium and determined by familiar methods. The experimentation here involved related especially to a *form of apparatus* well adapted to the combustion and resulted in the vertical combustion-tube described in the immediate context. It was further made to embrace several features concerning the absorption and determination.

1. *The Apparatus.*

The hydrocarbon is contained in a small flask of about 100 cc. capacity of the form shown in the sketch accompanying at V. It is connected at H with a supply of sulphur-free hydrogen. The outlet beyond the stopcock S is connected with the Y-tube attached to the arm B of the combustion-tube. The bulb on the exit-tube serves to prevent the spurting of condensate into the burner, which becomes possible when heat is required to assist the vaporizing.

The combustion-tube is shown in the essential features in the sketch. The Y-tube E A carries the burner, as seen, at P. The latter is a platinum piece slipped gas-tight over the glass tube. The burner-tube is joined by a short piece of rubber tubing to the arm B. At T is the tip for the pilot-flame. It is likewise of platinum, and is fused into a glass carrying-tube in the position indicated. In each arm, but not shown in the drawing, is a coil of platinum foil. It extends from the stopper nearly to the center of the combustion-tube. The arm-space is filled as completely as possible, only room required for the free passage of the burners being left. The upper end of the combustion-tube is connected



with the oxygen supply. The gas is passed for purification through a calcium chloride tower filled with pieces of caustic soda. Beside this jar stands a second charged in the same manner and serves for the purification of the air forced in at A. The connections on the jars are such that at the end of the combustion air may be turned into the apparatus from above, through the oxygen jar, for the purpose of aspiration, without disconnecting at any point.

The hydrogen for the pilot-flame is purified by passage through a small wash-bottle containing a solution of caustic soda. The arrangement is further required in aiding the regulation of the flow of gas. To observe the rate of the oxygen supply and deliver it comparatively dry to the purifying apparatus, thus prolonging the serviceability of the latter, the gas passes from the holder first through glycerol.

The combustion-tube is wrapped in asbestos cloth for protection against drafts, a small opening only being left opposite the flames to permit of their observation. In the coolest part of the tube, the arm, a dangerous accumulation of water may take place. Warming becomes therefore necessary and is efficiently and automatically accomplished by the rolls of platinum foil already referred to. In this form the gas combustion-tube has proven itself well adapted to its purpose; the cracking of the tube in service is rare and then usually the result of inadvertence.

### *2. The Combustion.*

The sample of benzene, about 5 grams, having been weighed in the vaporizer and all connections established, the apparatus is first filled with oxygen. The pilot-flame tube is withdrawn, a small flame started and the burner returned to its position in the combustion-tube. When first inserted, the flame must be larger than it is expected to maintain it, otherwise by the pressure existing in the tube, it will be so reduced in size as to be extinguished by the draft in the apparatus. The flame is adjusted to the smallest possible size consistent with keeping it alive. Care is taken to so place it that it is close to the edge of the burner-tip and will thus ignite the vapors instantly upon their arrival. With the arm *A* of the burner-tube and the stop-cock *S* closed, the hydrogen is turned into the vaporizer and thence cautiously admitted to the burner. Due to the downward movement of the oxygen, the vapors ignite even before reaching the tip of the burner, if the rate of admission is a little too slow. The flame appears at the tip brilliantly luminous. Increasing its size somewhat, air is admitted and the combustion continued with a half-luminous flame about 1 inch in length. Since some variation in the pressure of the gas entering the burner is scarcely to be avoided, the operation requires some oversight. The complete disappearance of benzene from the

gases supplied to the burner may be sharply detected by the appearance of the flame. A perfectly non-luminous flame denotes with certainty the end of the combustion. The stop-cock *S* is then closed, the pilot-flame extinguished, the oxygen turned off, and the passage of air through *A* continued for a few minutes. *A* is then closed and the air turned into the upper end of the combustion-tube by the simple setting of the stop-cocks on the air and the oxygen drying jars.

The combustion of 5 grams of benzene may be accomplished in about three hours. This applies to 90 and 100 per cent. benzene; light oil, with its less volatile constituents, requires a longer period. Warming the vaporizer hastens the operation and is necessary to completion of the process within a reasonable time.

### 3. *The Absorption.*

The gases and vapors leaving the combustion-tube contain the sulphur of the sample mainly as sulphur dioxide, but doubtless contain some sulphur trioxide as well. Mabery<sup>1</sup> states that in the form of apparatus devised by him for a somewhat similar purpose, the sulphur is contained wholly as sulphur trioxide notwithstanding the combustion was carried out in air, with the latter, however, in enormous excess. Special tests upon the gases from the above combustion apparatus detected sulphur dioxide unmistakably in large quantity. Several of the familiar absorbing media for the sulphur oxides were experimented upon and brominated sodium carbonate adopted for gravimetric determinations. The much more expeditious volumetric method of Mabery,<sup>2</sup> who used fractional normal alkali for absorption, was made the subject of some experiments.

In all cases glass-stoppered wash-bottles of about 250 cc. capacity were employed as receptacles for the absorber. Two were found adequate to the ordinary purpose.

The *sodium carbonate* and *bromine mixture* for absorption contained 25 grams of the purified crystallized salt dissolved in 110 cc. of water. The solution was distributed in equal volume between the two bottles. To the first was added more than an excess of bromine in saturated aqueous solution to oxidize the whole of the sulphur to be absorbed, assuming it present entirely in the form of sulphur dioxide. Ten cc. of the bromine solution

<sup>1</sup> Am. Ch. J. 18, 211.

<sup>2</sup> Pr. Am. Acad., Vol. 30.

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<sup>1</sup> Am. Ch. J. 18, 211.

<sup>2</sup> Pr. Am. Acad., Vol. 30.



are abundant for percentages up to 1.0. In each succeeding bottle of the absorber one-half the above quantity suffices.

With the carbonate-bromine absorber, as with all others tried, the formation of white fumes in the atmosphere of the absorbing bottles is a matter well-known to those who have dealt with the problem of the oxidation and absorption of the sulphur oxides, but perhaps still calling for some comment in this connection.

In all cases the fuming was most marked at the beginning of the combustion, at a time therefore when the vapors were most highly charged with sulphur in the form of carbon disulphide. Further, the higher the percentage of sulphur, the more voluminous the fume-formation, confirming the conclusion from the first observation that the fumes are carriers of sulphur. The subject is mentioned thus in some detail as emphasizing the necessity of a complete suppression of the fumes within the absorber if the utmost accuracy is to be attained. The accomplishment of this refinement, with conditions as set forth, has as yet not been fully realized in any simple manner. The limited and intermittent work which it has thus far been possible to devote to this phase of the determination has shown that, with an absorber made up of as many as four wash-bottles and with benzene samples of about 0.50 per cent. carbon disulphide, in the third and fourth bottles as a rule, the quantity of sulphur absorbed is practically the same, and an amount corresponding to somewhat less than 1 mg. of barium sulphate. Although numerous other devices (than increasing the number of absorbing bottles) for the promotion of extent and time of contact by the combustion gases with the absorber have been applied in conjunction with most of the practically available absorbing reagents, little or no better results than just indicated have been obtained. For technical purposes, however, this efficiency fully satisfies all requirements. The loss of sulphur sustained, by the use of two absorbing bottles as practiced, is not greatly beyond the limit of experimental error.

The use of *N/50 sodium hydroxide* gave, in the analysis of the 90 and 100 per cent. benzenes first experimented with very satisfactory results. Later efforts to apply the method to crude benzenes were unsuccessful. Time has not yet been available to determine the point of difficulty. The absorbing apparatus was composed in this instance likewise of two bottles each charged

with alkali in excess to the extent of 15 to 20 per cent. of the possible maximum requirement. Usually, about 0.5 cc. of the N/50 sodium hydroxide in the second bottle was used, and represents 0.003 per cent., with a total percentage, as above, of about 0.40.

#### 4. *Determination of the Sulphur.*

The *gravimetric* determinations were made with the usual precautions current for accurate work.

For the *volumetric* method, as already stated, N/50 sodium hydroxide was contained in the absorbing apparatus. To determine the excess of alkali N/10 sulphuric acid was found most practicable. Since the sulphur is present partly as sulphite, before titration the solution was treated with a few cubic centimeters of neutralized hydrogen peroxide; 5 to 6 cc. of a 2 per cent. solution sufficed for the main portion. The contents of the second bottle were treated with half the amount. The titrations were made in the absorption bottles, and with methyl orange as indicator.

However determined, attention need scarcely be called to the necessity of recovering the sulphuric acid remaining after the combustion upon the walls of the tube. When special accuracy is an object, the residues left in the vaporizer, especially by crude benzene, become a consideration.

#### 5. *Comparison of the Results Obtained.*

The results in the table following were from combustion of the same sample of benzene and, as noted, by both methods of determination.

#### GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS COMPARED.

<i>Method.</i>			
No.	Grav.	Vol.	No.
2	0.379	0.376	8
3	0.350	0.345	9
4	0.378	0.379	10
5	0.370	.....	...
6	0.370	.....	...
Average, 0.370		0.367	

Very satisfactory determinations have also been made with benzene containing as much as 5 per cent. carbon disulphide, the results being concordant within 0.10 per cent.

Insuring perfect and convenient combustion, the apparatus could be extended in its application to the determination of total sulphur in gases and vapors of whatever description. Fuel and illuminating gases are here in mind. It could further doubtless be made to lend itself in many instances advantageously to sulphur determinations in the ultimate analysis of organic compounds.

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## THE SYSTEM LIME, GYPSUM, WATER, AT 25°.<sup>1</sup>

BY F. K. CAMERON AND J. M. BELL.

Received June 30, 1906.

THE three-component system—lime, sulphuric acid, water—has been studied in this laboratory by Cameron and Breazeale.<sup>2</sup> In this work the composition of solutions containing an excess of the acid has been investigated over a wide range of concentration. In all solutions up to 300 grams of  $\text{SO}_3$  per liter the stable solid phase is gypsum. We have investigated the composition of solutions in which the lime has been in excess of the acid.

Two series of solutions have been prepared, one, various lime solutions to which solid gypsum has been added, and the other, various gypsum solutions to which lime has been added. These bottles were put in the thermostat at 25° and were rotated constantly for a period of two weeks. At the end of this time known volumes were analyzed for lime and for sulphuric acid. These results are given in the following table:

TABLE I.

$\text{SO}_3$ per liter. Grams.	$\text{CaO}$ per liter. Grams.	Solid phase.
0.0	1.166	$\text{Ca(OH)}_2$
0.230	1.302	"
0.392	1.424	"
0.562	1.608	"
0.714	1.742	"
0.934	1.876	$\text{Ca(OH)}_2, \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
0.961	1.612	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
1.013	1.320	"
1.090	1.112	"
1.128	0.966	"
1.194	0.898	"
1.251	0.875	"

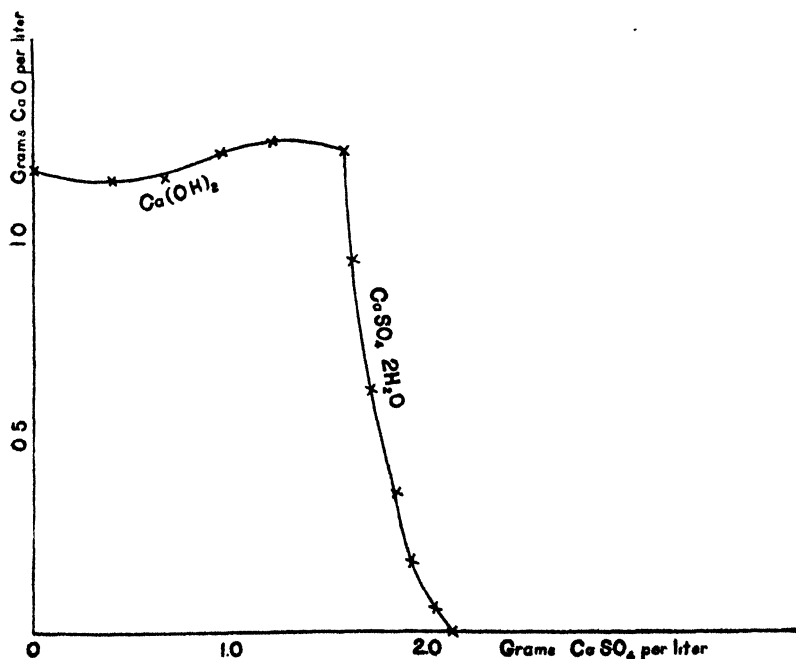
<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> J. Physic. Chem. 7, 571 (1903).

The results in the above table have been calculated to the amounts of calcium sulphate and of lime in the solution and are given in Table II. They are charted in the accompanying diagram.

TABLE II.

CaSO <sub>4</sub> per liter. Grams	CaO per liter. Grams.	Solid phase.
0.0	1.166	Ca(OH) <sub>2</sub>
0.391	1.141	"
0.666	1.150	"
0.955	1.215	"
1.214	1.242	"
1.588	1.222	Ca(OH) <sub>2</sub> , CaSO <sub>4</sub> ·2H <sub>2</sub> O
1.634	0.939	CaSO <sub>4</sub> ·2H <sub>2</sub> O
1.722	0.611	"
1.853	0.349	"
1.918	0.176	"
2.030	0.062	"
2.126	0.0	"



These figures indicate that the solubility of lime in gypsum solutions is constant within a few per cent., the solubility being greater in the more concentrated solutions. In lime solutions,

however, the solubility of gypsum decreases regularly as the amount of lime in solution increases.

BUREAU OF SOILS,  
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WASHINGTON, D. C.

## THE PHOSPHATES OF CALCIUM, III; SUPERPHOSPHATE.<sup>1</sup>

BY F. K. CAMERON AND J. M. BELL.

Received June 28, 1906

In former papers<sup>2</sup> from this laboratory, the three-component system—lime, phosphoric acid, water—has been investigated at 25°. It was found that there are three solubility curves, one representing solutions in equilibrium with monocalcium phosphate,  $(\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O})$ , one representing solutions in equilibrium with dicalcium phosphate,  $(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})$ , and the third representing solutions in equilibrium with a series of solid solutions. The compositions of these solid solutions extend from pure lime to a solution of nearly the same composition as dicalcium phosphate. Another three-component system—lime, sulphuric acid, water—has been studied in this laboratory.<sup>3</sup> The composition of solutions which are acid, *i. e.*, those in which sulphuric acid is in excess of lime, has been published in the former paper, while the composition of solutions which are alkaline has been investigated in the second paper. Only one solid phase was found in this first investigation, *viz.*, gypsum  $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ . Had that investigation extended to more concentrated solutions of sulphuric acid, another solid phase, anhydrite  $(\text{CaSO}_4)$ , would undoubtedly have been found. In the case of the alkaline solutions, two solid phases were found, calcium hydroxide and gypsum. In solutions containing less than 1.22 grams of free lime per liter the solid phase was found to be calcium hydroxide.

This present investigation deals with the four-component system—lime, phosphoric acid, sulphuric acid, water—the essential constituents of the so-called “superphosphates.”

A complete representation of the conditions obtaining in any four-component system can be attained only by the use of a space

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Cameron and Seidell: *This Journal*, 27, 1503 (1905); Cameron and Bell: *Ibid.*, 27, 1512 (1905).

<sup>3</sup> Cameron and Breazeale: *J. Physic. Chem.* 7, 571 (1903); Cameron and Bell: *This Journal*, 28, 1220 (1906).

model. Such a space model for this four-component system, would have as axes, the amounts of lime, sulphuric anhydride, and phosphoric anhydride per liter of solution. With the densities known, the amount of water in these solutions can be computed. However, this representation is cumbersome and so we have represented the results on one of the projections of this space model, *viz.*, on the coordinate plane bounded by the  $\text{SO}_3$ -axis and by the  $\text{P}_2\text{O}_5$ -axis. In other words, we have used a plane diagram representing all the conditions, with the exception of the lime content of the solutions. These conditions are described in the accompanying diagram (Fig. 1), in which some of the fields are so narrow as to necessitate their distortion in order to show plainly the regions involved.

In (Fig. 1) O represents a saturated solution of lime in water. On the OX axis, A represents the solution in equilibrium with dicalcium phosphate and the limiting solid solution; B represents the solution saturated with respect to both dicalcium phosphate and monocalcium phosphate. On the other axis, C represents the solution saturated with both calcium hydroxide and gypsum, and D the solution in equilibrium with both gypsum and anhydrite. The positions of the points A, B, C have been found by direct experiment, while the position of the point D has been determined in an indirect way. This method was adopted, since the change of gypsum to anhydrite, or *vice versa*, has been shown to be very slow. In his work on the various forms of calcium sulphate, van't Hoff<sup>1</sup> has shown that at vapor-pressures lower than 17.5 mm. at 25°, gypsum is transformed to natural anhydrite, and above that pressure the reverse change takes place. Applying this result to the present problem, we have determined the strength of sulphuric acid which has a vapor-pressure of 17.5 mm. when saturated with gypsum. The sulphuric acid solution having this vapor-pressure has been found, from the results of Richards,<sup>2</sup> to have a density of 1.235. This solution contains 25.71 per cent.  $\text{SO}_3$ ,<sup>3</sup> or 317.5 grams  $\text{SO}_3$  per liter. In this consideration no correction is made for the effect of the calcium sulphate in solution on the vapor-pressure, a correction which would be very small because of the low solubility of gypsum in sulphuric acid

<sup>1</sup> Sitzungsber. Akad. Wiss. Berlin, 1901, 1140.

<sup>2</sup> Pr. Am. Acad. 33, 23 (1897-98).

<sup>3</sup> Fresenius "Quantitative Analysis," 1899, p. 676.

Fig. 2.

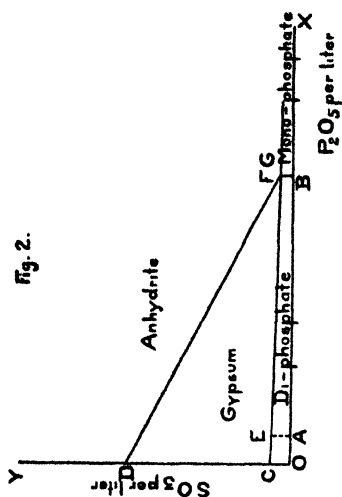


Fig. 1 25°C.

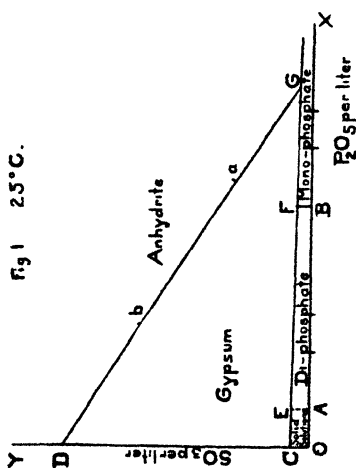


Fig. 4 66°C.

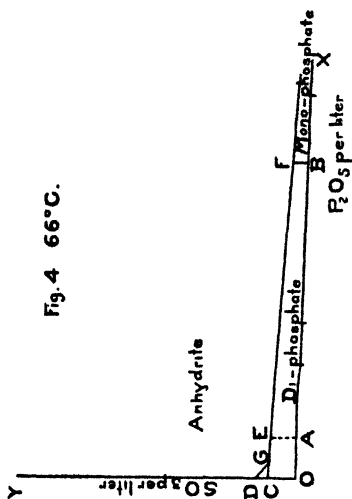
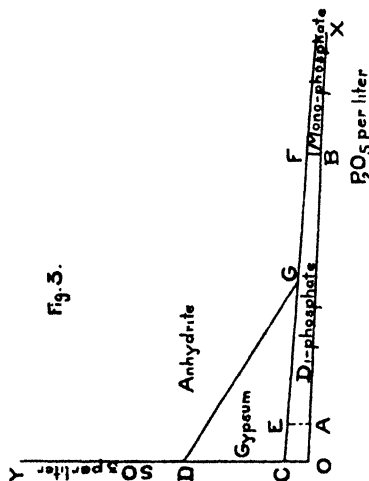


Fig. 3.



of that strength. This solubility has been estimated by extrapolation from the results of Cameron and Breazeale<sup>1</sup> to be approximately 1 gram of calcium sulphate per liter of solution.

The determination of the possible fields has been investigated by adding small quantities of sulphuric acid to various solutions represented on the diagram by points on the line OX. In all cases the addition of a little sulphuric acid causes a white precipitate which upon microscopic analysis proved to be gypsum.

<sup>1</sup> Loc. cit.

This indicates that the fields over which the phosphates of calcium can exist are very narrow indeed. An analysis for sulphates was made of three of these solutions, one about midway between A and B in the diagram, one very near B, and the third on BX. The sulphuric acid content of these three solutions was found to be 0.9, 0.6 and 0.3 gram  $\text{SO}_3$  per liter respectively, and hence the line C E F G lies very close to OX, the two lines converging as we pass to the right. Analyses of some of these solutions have been made by Cameron and Seidell,<sup>1</sup> their lime content and phosphoric acid content being practically the same when no gypsum is present as it is when the solution is saturated with respect to gypsum. These solutions lie on the line E F, near the point E. Thus it is evident that the presence of gypsum has no appreciable effect on either the lime content or the phosphoric acid content of the solutions, and as the amount of the sulphate in solution is greater in this region than it is farther to the right, it is apparent that the solutions near F and to the right of F have the same lime content and phosphoric acid content as those on the axis OX. The positions of the points E and F have therefore been taken as almost identical with the positions of A and B.

Finally, the position of the line forming the boundary between the gypsum and anhydrite fields has been found. From the work of van't Hoff, which has been cited above, the vapor-pressure at which gypsum and anhydrite remain in equilibrium at  $25^\circ$ , is 17.5 mm. Consequently, the solutions on the diagram which have that vapor-pressure are on the boundary line between the two fields. In these determinations we have not attempted to obtain equilibrium conditions but we have found whether various solutions had vapor-pressures above or below this value. This has been accomplished by placing a weighed solution (25 grams of solution in a weighing-bottle) known to have this vapor-pressure in a bottle containing the unknown solution. After a time the former solution was again weighed, and from the loss or gain it has been found whether the vapor-pressure of the unknown solution was above or below 17.5 mm. In this way the position of the point G has been determined, at which point gypsum, anhydrite and monocalcium phosphate co-exist as solids in equilibrium with a solution. Also we have found the position of two points,

<sup>1</sup> This Journal, 26, 1461 (1904).



*a* and *b*, along the line D G which separates the gypsum field from the anhydrite field.

To determine the point G various solutions along BX, whose vapor-pressure are not different from those along F G, have been investigated with the following results: The solution containing 485 grams  $P_2O_5$  per liter caused an increase in weight of 0.080 gram in two days; the solution containing 563 grams  $P_2O_5$  per liter caused a decrease in weight of 0.026 gram in two days. As these experiments were carried on under identical conditions, we have interpolated to find that solution which should show no change in weight. This has been found to contain 545 grams  $P_2O_5$  per liter, and therefore G is determined. The positions of the points *a* and *b* have been found by similar pairs of determinations. The composition of the solution at *a* is 350 grams  $P_2O_5$  per liter and 120 grams  $SO_3$  per liter, and the composition at *b* is 150 grams  $P_2O_5$  per liter and 275 grams  $SO_3$  per liter.

The following table gives the data concerning the invariant or "constant" solutions at 25°.

Point.	$P_2O_5$ per liter. Grams.	$SO_3$ per liter. Grams.	CaO per liter. Grams.	Solid phases present.
O	0	0	1.17	$Ca(OH)_2$ .
A	3	0	1.5	Solid solution; $CaHPO_4 \cdot 2H_2O$ .
B	317	0	77.	$CaH_4(PO_4)_2 \cdot H_2O$ ; $CaHPO_4 \cdot 2H_2O$ .
C	0	0.9	1.9	$Ca(OH)_2$ ; $CaSO_4 \cdot 2H_2O$ .
D	0	317.5	1.	$CaSO_4 \cdot 2H_2O$ ; $CaSO_4$ .
E	3	0.9	1.5	Solid solution; $CaSO_4 \cdot 2H_2O$ ; $CaHPO_4 \cdot 2H_2O$ .
F	317	0.6	77.	$CaSO_4 \cdot 2H_2O$ ; $CaHPO_4 \cdot 2H_2O$ ; $CaH_4(PO_4)_2 \cdot H_2O$ .
G	545	0.2	38.	$CaSO_4 \cdot 2H_2O$ ; $CaSO_4$ ; $CaH_4(PO_4)_2 \cdot H_2O$ .

To describe the conditions which obtain at any other temperature than 25° it is necessary to determine how the various points on the diagram are affected by changes of temperature, and also to determine whether any new solid phases appear. In the present case a microscopic examination of the crystals formed at the higher temperature has revealed no new types and it is therefore probable that there are no new solid phases. Above the temperature 66° the solid gypsum, stable at all lower temperatures, becomes unstable and therefore does not appear on the diagram representing the conditions at 66°. It has been found by experiment that the points B and F move to the right with rising temperature. In other words the two phosphates of calcium co-exist in solutions which become richer in phosphoric

acid as the temperature increases. The points E and A have not been investigated at any temperature other than  $25^{\circ}$ , but it is certain from qualitative experiments that at higher temperatures there is a field for solid solutions just as there is at  $25^{\circ}$ . This has been indicated in Figs. 2, 3 and 4 by the dotted line E A. The direction in which the point D moves with change of temperature can be predicted from the results of van't Hoff<sup>1</sup> upon the vapor-pressure at which gypsum and anhydrite exist in equilibrium.

The composition of sulphuric acid solutions which have the same vapor-pressures at  $10^{\circ}$ ,  $25^{\circ}$  and  $35^{\circ}$  have been computed from the data upon the vapor-pressures of these solutions,<sup>2</sup> with the following results. It is apparent that the point D approaches C with rise of temperature.

Temperature, °C.	Vapor pressure at which gypsum and anhydrite co-exist	Composition of $H_2SO_4$ with same vapor-pres- sures in per cent. $H_2SO_4$ .
10 .....	5.79	37.6
25 .....	17.5	31.5
35 .....	32.2	28.5
66 .....	150.	0.

At  $66^{\circ}$  gypsum and anhydrite co-exist in contact with their own solution in water. The presence of lime, whose solubility in water at this temperature is less than 1 gram per liter, will lower this temperature very slightly. Similarly along the line C E G F, the point G is continually moving towards the point C. Consequently, it is evident that the field for gypsum disappears at a temperature of  $66^{\circ}$  and anhydrite becomes the stable solid over a very great range of solutions.

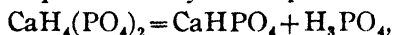
It is evident that at some temperature intermediate between  $25^{\circ}$  and  $66^{\circ}$  the point F, which is moving to the right with increasing temperature, will meet the point G which is moving to the left. At this point we have a sextuple point, or six phases, vapor, solution, and the four solids anhydrite, gypsum, mono- and dicalcium phosphates. This state of affairs can exist at only one temperature and one vapor-pressure. This is shown diagrammatically in Fig. 2. As the temperature increases still further, the points D and G approach C, and Fig. 3 illustrates the state of affairs at some temperature below  $66^{\circ}$ . At the temperature  $66^{\circ}$  the field for gypsum disappears altogether.

From the preceding results and diagram (Fig. 1) the effect of

<sup>1</sup> Loc. cit.

<sup>2</sup> Landolt and Börnstein: *Phys.-Chem. Tabellen* (1905), pp. 166-167.

water upon a mixture of the salts may be deduced. We shall neglect in the following consideration the effect of substances other than gypsum and monocalcium phosphate, which substances are nearly always present in commercial superphosphates, *viz.*, ferric phosphate, aluminum phosphate, calcium chloride or fluoride, etc. All these substances will have some influence upon the positions of the various points and lines in the above diagram but if their amount is small we may neglect their influence. Let us leach a superphosphate composed of gypsum and monocalcium phosphate at 25°. The addition of water to monocalcium phosphate crystals causes a partial change to dicalcium phosphate and a solution saturated with respect to both phosphates. A small amount of gypsum will also pass into the solution. If water be added to this solution, or if the solution be drained away and fresh water added, more of the monocalcium phosphate will disappear and dicalcium phosphate will be formed. The net effect of this leaching is to wash out some free phosphoric acid, together with considerable quantities of calcium and a very small quantity of gypsum. If the addition of water is rapid, the time for this change may be very short indeed. During this change the composition of the solution is represented by the point F of Fig. 1, and if equilibrium conditions are obtained, the composition of the solution will remain constant until *all* the monocalcium phosphate disappears. It will be observed that the greater part of the original calcium phosphate has been removed. This may be partially represented by the equation



all the phosphoric acid in excess of the compound  $\text{CaHPO}_4$  being leached away, together with a considerable amount of the diphosphate, which is dissolved. Upon the removal of some of the solution and dilution of the residue by fresh water, the composition of the leachings will change rapidly until the point E is reached. Here another change takes place, the crystalline dicalcium phosphate giving up phosphoric acid, which carries some of the phosphate into solution. The solid changes to a solid solution of lime and phosphoric acid and upon continued leaching this solid solution changes gradually to that solid solution which in saturated gypsum solutions dissolves unchanged, *i. e.*, the ratio of lime and phosphoric acid which have gone into solution is the same as in the solid solution. Over this range of concentrations

gypsum has a much higher solubility and it will probably disappear before the solid solutions have all disappeared.

We may therefore divide the process of leaching of superphosphate roughly into four stages: First, monocalcium phosphate disappears, and solid dicalcium phosphate and a solution of phosphoric acid containing much of the lime are formed. The weight of the resulting dicalcium phosphate is less than one-half of the original monocalcium phosphate. Very little gypsum has gone into solution at this stage. The second stage consists in the complete change of dicalcium phosphate into an amorphous solid solution, and very much more gypsum goes into solution. The third stage in the leaching process is the gradual change in the solid solution to one containing relatively less phosphoric acid and more lime. The liquid solutions are now quite dilute and consequently gypsum will dissolve freely, and it is certain that the gypsum will all be washed away before the calcium phosphate (as solid solution) has been all dissolved. The fourth stage consists in the slow solution in water of a relatively insoluble solid solution of lime in phosphoric acid, which contains relatively more lime than would be required by the formula  $\text{Ca}_3(\text{PO}_4)_2$ .

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## THE COMPOSITION OF THE DRAINAGE WATERS OF SOME ALKALI TRACTS.<sup>1</sup>

BY FRANK K. CAMERON.

Received June 28, 1906.

IN the reclamation of an alkali tract the analysis of the drainage water is the most ready method of following the changes taking place within the soil. That the nature of the drainage water and the changes which it may undergo are problems of great practical importance is obvious when it is considered that agricultural plants display such marked difference in their tolerance of different salts and salt mixtures in their nutrient media. It is also important to note that a study of drainage water not only furnishes a clue to the nature of the soil solution in the land from which it flows, but that it may have an important bearing on the management of neighboring lands upon which it may be desirable

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to use the water again for irrigation or where the land may be affected through seepage.

It has popularly been supposed that the composition of a drainage water from an alkaline soil could be easily predicted from a knowledge of the respective solubilities of the salts composing the alkali, and even the recent literature contains discussions of this subject based upon the erroneous notion that the several components of a mixture will necessarily be removed in the order of the individual solubilities. That such is not the case, but that the relation of the vapor-pressures of the solution and of the solid components, the formation of new molecular species (such as so-called double salts), as well as some other possible factors in each individual case, must be considered, has been known, though generally ignored, by chemists and soil investigators. That the composition of the resulting solution with respect to the dissolved constituents remains constant so long as no one of the solid components disappears is well illustrated in a simple case, a mixture of sodium nitrate and potassium nitrate. If such a mixture be treated by successive portions of water, assuming, of course, that the temperature be kept constant, the composition of the several resulting solutions will be exactly the same so long as both solid salts remain in the mixture. Precisely the same sort of thing will happen with any mixture of solids, no matter how complex the course of the washing out of a mixture of salts by water, the composition of the solution which results will depend only on the solid phases which are present and not on their relative amounts. When any one of the solid phases becomes completely washed out, the composition of the solution will change.

The accumulation of alkali at the surface of soils is due mainly to the evaporation of seepage waters from lower levels. These seepage waters will in all probability have a constant composition as the water has become saturated with respect to all the constituents of the salts in the lower depths. In the converse process of washing out, the solution should have a constant composition until some one or more of the salts completely disappears. This has actually been observed in the investigations of this Bureau.

A tract of land near Salt Lake City, Utah, has been under process of reclamation, tile drains having been installed and the land leveled and frequently flooded. When reclamation was

undertaken, the surface soil of this tract contained, on the average, upward of 2.7 per cent. soluble salts, while it now contains less than 0.3 per cent. soluble salts. At frequent intervals since the installation of the drains, samples of the water from the outlet weir of the drainage system have been forwarded to the laboratory for analysis. The composition of the principal dissolved mineral constituents, at several different dates, is given in the following table, the analyses up to September, 1904, having been made by Mr. Bailey E. Brown, and the subsequent analyses by Mr. W. C. Taber.

TABLE I.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR SALT LAKE CITY, UTAH.

Date	Ca. Per cent	Mg. Per cent	Na. Per cent.	K. Per cent.	SO <sub>4</sub> Per cent.	Cl. Per cent.	HCO <sub>3</sub> Per cent.	CO <sub>3</sub> Per cent	Parts per million in solution.
1902 Sep.	0.38	0.50	33.74	2.04	18.62	37.76	6.49	0.48	18035
Oct.	0.23	0.78	34.73	1.49	19.14	39.52	5.06	0.29	17915
Nov.	0.19	0.74	34.42	1.40	18.61	40.46	3.95	0.23	19905
1903 May	0.38	0.61	34.48	0.84	29.90	38.19	4.30	0.25	18752
June	0.45	0.85	34.18	1.09	17.52	41.00	4.23	0.42	21099
July	0.50	0.80	34.06	1.25	18.24	40.24	4.67	0.30	19089
Aug.	0.35	0.90	34.40	1.12	17.15	42.37	3.48	0.16	26060
Sep.	0.49	0.72	34.54	1.24	17.31	42.02	3.36	0.33	22240
Oct.	0.47	1.02	33.43	1.52	16.08	43.28	3.33	0.30	19020
Dec.	1.25	0.70	32.62	1.69	19.89	37.44	6.18	0.22	12966
1904 Jan.	0.15	0.75	33.93	1.26	20.08	36.64	6.94	0.25	11334
Feb.	0.34	0.78	34.59	0.70	18.95	40.15	4.49	...	.....
Mar.	0.29	0.77	34.57	1.28	16.31	42.28	3.81	0.19	21006
Apr.	0.29	0.70	34.28	1.37	20.93	38.04	3.33	1.06	16372
May	0.71	0.74	26.92	4.01	21.26	40.93	4.05	1.38	12677
June	0.37	0.70	32.60	3.55	19.94	37.42	4.05	1.37	12695
Aug	0.37	0.86	33.85	2.13	17.12	41.31	3.20	1.16	15073
Sep.	0.42	0.79	34.10	1.35	19.01	39.85	4.11	0.37	15717
Oct.	1.04	0.60	33.01	1.86	21.42	36.63	4.68	0.76	11623
1905 Feb.	0.32	0.67	33.59	0.99	22.30	33.32	8.45	0.36	8235
Mar.	0.31	0.66	33.46	1.30	21.60	33.86	8.46	0.35	8455
Apr.	0.35	0.65	34.20	1.01	20.03	36.99	6.22	0.55	10701
May	0.45	0.86	33.43	1.20	20.59	36.04	6.96	0.47	9569
June	0.40	0.94	34.05	1.32	20.89	35.85	5.71	0.84	10612
July	0.32	0.69	33.67	1.30	21.17	34.94	7.23	0.68	8763
Aug.	0.35	1.04	33.12	1.58	21.58	35.92	5.72	0.99	9000
Sep.	0.42	0.82	33.39	1.26	21.18	34.85	7.41	0.67	8992
1906 Jan	0.55	0.84	33.12	1.11	21.10	34.35	8.57	0.36	8401
Apr.	0.32	0.77	34.03	1.09	19.84	37.40	6.03	0.52	11531

It will be observed that the variations of the several constituents, within an interval of nearly four years, are very small,

such differences as do appear being readily attributable to the relatively small changes in the actual concentrations of the drainage water at different times, produced by the addition of large quantities of water in flooding, some of which reached the tiles before coming into equilibrium with the soil components.

In Tables II, III and IV are given the data obtained with drainage waters from a tract near Fresno, California, a tract near North Yakima, Washington, and a tract near Billings, Montana. In these cases it has not been considered necessary to have such complete analyses, over the entire time which the reclamation has been progressing, so that the data given apply to much shorter intervals than in the case of the Swan tract. They furnish, nevertheless, interesting examples of the same character.

TABLE II.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR FRESNO, CALIFORNIA.

Date, 1903.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K Per cent.	SO <sub>4</sub> . Per cent.	Cl. Per cent.	HCO <sub>3</sub> . Per cent.	CO <sub>3</sub> . Per cent.	Parts per million in solution.
March 28	8.90	3.77	11.78	2.66	12.23	6.66	54.00	.....	450
April 25	6.91	6.06	7.88	2.18	4.85	8.85	63.27	.....	824
May 2	3.59	4.15	16.35	1.75	2.39	8.95	60.99	1.83	1251
May 9	3.57	3.64	20.49	1.58	2.06	9.62	51.82	7.22	1454
May 16	3.58	3.76	19.72	1.44	1.88	9.69	54.79	5.14	1592
May 23	5.36	4.28	15.47	1.76	3.06	10.73	59.34	.....	1306
May 30	2.07	3.47	23.55	2.00	7.01	10.55	40.63	10.57	1639
June 6	3.01	3.15	22.84	2.35	6.45	11.79	40.50	9.79	1495
June 13	3.24	2.96	22.70	2.19	3.91	13.35	43.32	8.29	1048
June 20	3.81	3.21	21.82	1.87	2.79	11.78	54.19	.....	1494
June 21	3.20	3.38	21.09	2.82	2.63	9.88	56.96	.....	1062
July 4	3.06	2.27	20.82	2.63	4.98	6.12	57.21	2.97	1143
July 11	3.60	1.69	23.04	3.77	6.38	18.09	39.32	3.90	768

TABLE III.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR NORTH YAKIMA, WASHINGTON.

Date, 1903.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO <sub>4</sub> . Per cent.	Cl. Per cent.	HCO <sub>3</sub> . Per cent.	CO <sub>3</sub> . Per cent.	Parts per million in solution.
Aug. 1	4.93	5.26	12.91	4.09	20.06	4.85	47.91	.....	1440
Aug. 9	8.43	6.46	7.06	4.27	17.57	7.30	48.87	.....	1684
Aug. 15	7.58	3.23	14.19	4.68	24.51	6.47	36.95	2.40	2162
Aug. 22	7.57	5.03	12.09	3.37	23.68	6.45	39.10	2.66	2166
Aug. 29	5.27	5.06	14.52	3.56	21.36	4.79	41.43	3.96	1460
Sep. 5	7.36	5.21	12.38	1.86	23.33	5.01	43.40	1.38	2092
Sep. 12	9.32	5.59	10.29	1.32	25.55	6.79	41.12	trace	2575
Sep. 19	4.80	10.91	0.33	0.56	26.06	5.94	46.21	2.43	1768
Sep. 26	5.05	4.98	14.44	3.49	15.18	5.21	47.31	4.32	1343
Oct. 3	5.09	0.41	15.36	2.20	14.12	0.47	54.23	.....	1451

TABLE IV.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR BILLINGS, MONTANA.

Date.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO <sub>4</sub> . Per cent.	Cl. Per cent.	HCO <sub>3</sub> . Per cent.	CO <sub>3</sub> . Per cent.	Parts per million in solution.
1905 June	2.0	5.84	20.44	0.45	65.98	1.57	3.65	0.07	22376
July	2.33	5.71	20.29	0.53	65.27	1.60	4.27	.....	15490
Aug.	3.25	5.36	19.45	0.82	63.53	1.79	5.80	.....	7841
1906 May	3.63	5.95	18.72	0.46	69.07	1.47	0.45	0.25	11950

The data just presented are believed to be of more than ordinary importance, because they so well illustrate the character of the results which may be anticipated in a large number of cases in actual field work. How long the practically constant percentage composition of the dissolved salts would continue in the drainage water under continued flooding it is, of course, difficult, if not impossible, to predict. It is reasonably certain that sooner or later some one or more of the solid components in the soil would be completely removed, barring absorption or some other special phenomena, and the nature of the solution might then be very materially altered. As a practical matter, however, it should be remembered that the persistence of the several solid phases of the alkali mixture does not necessarily mean that they are evenly distributed in the soil, and that while they may be determining the composition of the solution as it passes into the drain tiles, some of these solid phases may have been removed from the surface soil, which would then hold a solution of different character, in which latter crops could very well grow. This seems to be true, as there is evidence that crops can now be grown on some of these tracts, if proper cultural methods be maintained to prevent the subsequent capillary rise of the water added in flooding. It appears certain, however, that in such cases the land can not be truly regarded as finally reclaimed until the change in the composition of the drainage water shows that there has been a complete removal of some of the solid salts from that portion of the soil which feeds the drains.



# THE LIBERATION OF FORMALDEHYDE GAS FROM SOLUTION BY MEANS OF ITS ACTION ON POTASSIUM PERMANGANATE.

BY G. B. FRANKFORTER AND RODNEY M. WEST.

Received July 28, 1906.

As indicated in this Journal (27, 714), when strong formaldehyde is brought in contact with powdered potassium permanganate, a violent reaction takes place liberating carbon dioxide, formic acid, a large amount of formaldehyde gas and producing a large amount of heat. Experiments extending over a number of years have been made with the object of determining the ratio between the amount of formaldehyde liberated and the amount of heat produced, or in other words, the amount of heat produced by the oxidation of a known amount of formaldehyde gas. The results of a large number of experiments showed that it is extremely difficult to obtain concordant results. It was found that the condition of the permanganate, whether in crystal form or whether coarsely or finely powdered, made a great difference in the reaction. The strength of the formaldehyde solution and the rate of flow upon the permanganate likewise made a great difference both in the percentage of formaldehyde liberated and in the amount of heat produced. In fact, so many variables entered into the reaction that the calorific determinations were laid aside for the time and the conditions under which the greatest amount of formaldehyde gas could be liberated by potassium permanganate studied.

## DETERMINATION OF FORMALDEHYDE.

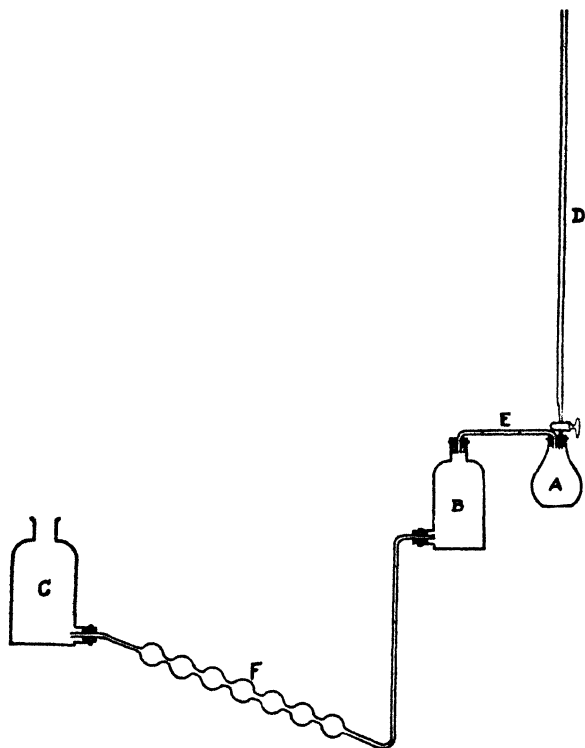
Several obstacles were encountered in the determination of the amount of formaldehyde gas liberated by means of potassium permanganate. One of the first difficulties was in retaining the formaldehyde gas so that it could be accurately determined. The evolution of gas is usually so violent that the ordinary gas-bag stop-cock is not large enough to allow the gas to escape without producing an enormous pressure upon the generator; or in case of absorption of the gas it is extremely difficult to absorb all the gas either by water or by ammonia.

Another difficulty was experienced in bringing the formaldehyde solution in contact with the permanganate. If the aldehyde is allowed to drop on the permanganate from a burette, a crater

of oxides of manganese is formed just where the aldehyde comes in contact with the permanganate, retaining the aldehyde so that after a short time the reaction almost stops. If, on the other hand, the formaldehyde is added all at once, the gas is liberated with explosive violence and at the same time the actual percentage of formaldehyde liberated is considerably less than when the formaldehyde solution is allowed to drop from a burette on the permanganate. In fact, several violent explosions were caused by adding strong formaldehyde solution to finely powdered permanganate. Frequently when 40 per cent. formaldehyde is slowly dropped on the powdered permanganate, a little flame is produced as each drop of formaldehyde strikes the powder. In this case the amount of formaldehyde is greatly diminished and the carbon dioxide greatly increased.

An attempt to overcome this violent reaction was made by diluting the formaldehyde with water. It was found, however, that while the addition of water modified the reaction, the quantity of formaldehyde gas was greatly diminished. Finally, the dilution of the permanganate by some inert substance was tried and found to give satisfactory results. The potassium permanganate was powdered and mixed with clean sand and the formaldehyde allowed to drop on this mixture. The sand prevented the formation of the crater of oxides of manganese. The formaldehyde percolated through the mixture and the reaction continued as long as the aldehyde was added and as long as there was unchanged permanganate left in the generator. As the gas is liberated from the solution by the heat of the reaction and as the specific heat of the sand is much less than that of water, more heat and hence more gas must necessarily be liberated by diluting the permanganate with sand than by diluting the formaldehyde solution with water. Notwithstanding the modifying effect of sand upon the above reaction, the change was still violent unless a large proportion of sand was used. It was found that a mixture of equal parts of sand and permanganate gave best results. With this proportion the reaction was violent but not to such an extent as to make the collection of the gas impossible.

Several forms of apparatus were tried. That indicated in Fig. 1 was adopted as giving satisfaction, whether the gas was collected in gas bags and measured or determined by absorption. A wide-mouth, short-neck flask *A* of about 200 cc. was fitted with



a double bored rubber stopper. Through one hole passed a burette for introducing a known quantity of formaldehyde. Through the other passed a delivery tube *E* of large diameter. This delivery tube was connected with an aspirator bottle *B* filled with water, one liter giving best results. The side neck of the aspirator bottle was connected with an absorption tube *F*. The absorption tube was so placed that the upper end was below the surface of the water in *B*, thus slightly diminishing the atmospheric pressure upon the gas. The other end of the absorption tube was connected with another aspirator bottle *C* which serves as a receiver in case the gas is not entirely absorbed as soon as it passes into *B*. If the reaction is very violent, forcing all of the water out of *B* into *C* by rapid liberation of gas, loss will be prevented by bubbling through the water in the absorption tube. At the end of the reaction the water is finally drawn back into *B*, but is prevented from being drawn over into *A* by the air which filled the generator at the beginning of the experiment. Usually,

the absorption-tube is unnecessary except as a connecting tube between *B* and *C*. When all the gaseous formaldehyde has been absorbed by the water, it is thoroughly mixed, measured and the formaldehyde determined. During the reaction the temperature in the generator is practically constant at the boiling-point of water.

In the following table of analyses the solution used was 37.8 per cent. formaldehyde and the permanganate used was mixed with an equal amount of sand. The quantity of water used in absorbing the gas was varied, but 500 to 1000 cc. seemed to give the best results when 50 cc. of the formaldehyde solution were used. With very large quantities of water the solution became so dilute as to make an exact determination of formaldehyde somewhat difficult

	KMnO <sub>4</sub> + Sand. Grams.	Formaldehyde solution. cc.	Volume of water used in absorption. cc	CH <sub>2</sub> O liberated. Per cent.
1 .....	100	50	1000	69.12
2 .....	100	50	1000	71.42
3 .....	100	50	1000	69.12
4 .....	100	50	1000	67.96
5 .....	150	50	1000	65.92
6 .....	150	50	1000	63.53
7 .....	200	50	1000	71.77
8 .....	200	50	1000	70.00
9 .....	200	50	1000	70.00
10 .....	200	50	1000	65.00
11 .....	200	50	1000	65.00
12 .....	200	50	500	64.53
13 .....	200	50	500	64.53
14 .....	200	50	500	64.53
15 .....	200	50	500	67.43
16 .....	200	50	500	67.53
17 .....	200	50	500	64.53
18 .....	200	50	500	62.21
19 .....	200	50	500	64.53

A large number of determinations were made, varying the time of reaction or the rate of flow of formaldehyde solution on the permanganate. The following table gives the average percentage of gas liberated:

Number of analyses.	Time of reaction. Minutes.	CH <sub>2</sub> O. Per cent.
3 .....	80	65.96
3 .....	60	68.06
6 .....	45	73.11
3 .....	30	74.56
2 .....	15	73.56
9 .....	10	70.48

In these determinations 200 grams of the mixture of sand and permanganate and 50 cc. of 38 per cent. formaldehyde were used. During the process a considerable quantity of water distilled over. The greater part of the water came from the formaldehyde solution; a small quantity was formed by the oxidation of the formaldehyde. Measurements showed that about 45 cc. distilled.

The above averages indicate that with the quantities of permanganate and formaldehyde used in these experiments, the best results were obtained by allowing thirty minutes to complete the reaction. When more than that is taken, the amount of formaldehyde liberated seems to decrease and the amount of carbon dioxide to increase. With less than thirty minutes to complete the reaction, the amount of formaldehyde decreases and the amount of carbon dioxide seems also to decrease. Determinations of both carbon dioxide and formic acid are now being made.

UNIVERSITY OF MINNESOTA.

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### NOTES.

*A Modification of the Hanging Drop Fluoride Test.*—The necessary apparatus consists of a test-tube of small bore and about 2 inches long (a litmus-paper bottle serves admirably), fitted with a rubber stopper. The latter carries a small bit of glass tubing, closed at one end and inserted in the bottom of the stopper so that the open end shall extend about 3 mm. into the tube.

The precipitate of calcium carbonate and calcium fluoride, ignited until nearly free from carbonate, is well mixed with about 0.1 gram of precipitated silica and introduced into the dry tube. The bit of glass tubing is nearly filled with a couple of drops of water, the bottom of the stopper wiped thoroughly dry, and the latter inserted into the tube immediately following the addition of 1 to 2 cc. strong sulphuric acid. Place the tube in a beaker of water at the boiling-point and maintain at this temperature for fifteen to thirty minutes. If the substance under examination contained any appreciable quantity of fluoride its presence will be promptly indicated by the formation of a heavy gelatinous ring that not infrequently completely fills the end of the tube in the stopper.

In the writer's estimation, this procedure is far preferable to the troublesome and occasionally somewhat uncertain etching

test usually employed. Furthermore, by simultaneously proceeding with tubes containing known amounts of fluoride, this process may be made roughly quantitative.

C. D. HOWARD.

*The Disposal of Ammonia, Tar and Gas from By-Product Coke Ovens.*—The writer's attention has been called to a review in the June number of the Journal, of the book entitled "A Short Treatise on the Destructive Distillation of Bituminous Coal," in which the reviewer draws some conclusions as to the disposal of coke oven by-products that hardly seem justified when the rapid development of these markets in recent years is considered, as well as their present status. The review questions whether the addition of a plant carbonizing 1,000 tons of coal daily, to the present by-product oven installation, producing approximately three and a quarter million gallons of tar and 3,500 net tons of ammonium sulphate per year, would not so depress the by-product market as to "deprive that type of construction not only in the new plants, but also in those previously erected, of the greater part, if not all, of the advantages resulting from its output of by-products."

The market for ammonia in all forms, including sulphate, has undergone an increase from 18,000 net tons of sulphate equivalent produced in 1899, to 54,664 net tons in 1904, or, roundly, 200 per cent. increase in five years. The average price has consistently risen during this addition and has shown to date no tendency to recede. As the imports of sulphate were 6,976 net tons in 1899, and 15,288 net tons in 1905, any apprehension as to a catastrophe in this particular industrial field by the addition of 3,500 tons to the home production may well be laid aside until needed. Such an installation as cited requires a year for its completion, which is ample notice for the market to adjust itself to requirements. To one who appreciates the vast field open to ammonium sulphate as a fertilizer, and who is aware that the United States, the greatest agricultural country in the world, now uses but one-third of the nitrogen used as a fertilizer in Germany, per unit of population, including the large nitrate of soda imports in both countries, such apprehensions seem idle.

The market for tar, it is true, furnishes more reasonable ground for conservatism. The tar from the 3,000 odd by-product coke

ovens now in existence in this country has practically all come on the market within the last ten years, there having been but 72 by-product ovens in 1895, according to Dr. Parker's report. The total production of coal tar from gas works and by-product ovens was 69,498,085 gallons in 1904, according to the same authority. Of this, 41,726,970 gallons or 60 per cent. was produced in the gas works, the balance, 27,771,115 gallons or 40 per cent. being produced in the by-product coke ovens; therefore the addition of the by-product coke oven tar to the existing gas works production represents at least 66 per cent. increase, besides that due to the extension of the gas production itself. As the Geological Survey reports above referred to were not issued as early as 1895, we have no accurate data on this point, but the report by Dr. Wm. B. Phillips in 1898 gives the production of tar in gas works for that year as 24,384,798 gallons. The amount in 1895 was assuredly less than this. Contrasting this figure, however, with the present production we see that an increase has taken place of approximately 200 per cent. up to and including 1904, and including 1905, it will approximate 250 per cent. increase. Under these conditions the value of the tar, quoted in 1898 at 3.7 cents per gallon by the above authority has fallen to 3.04 cents in 1904. This is a loss, to be sure, but it is by no means a serious one. It must be remembered that the first resort for the tar producers in a low market is to burn it as a fuel, for steam raising, etc., for which purpose it is equivalent to coal at a ratio of 5 pounds of tar for 8 pounds of coal. Therefore, where coal is worth \$3.75 per net ton, tar can be burned with equal economy at a cost of 3 cents per gallon, or where coal costs \$3.12, tar is worth 2.5 cents per gallon.

Even under the tremendous expansion that the coal tar manufacturing industry has undergone, prices in this country have never averaged as low as those prevailing in England and Germany. Nevertheless in these countries the by-product oven system is constantly gaining ground, and in Germany in particular is now far in the lead. A far greater proportion of the United States tar production goes into the manufacture of prepared roofing and for water-proofing than is the case in either of these other countries. A great and immediate increase in the tar production might conceivably so far modify these conditions as to cause American prices to approach the English figures,

but this would detract but little from the economic advantages of the by-product coke oven process.

It is therefore clear that, for both ammonia and tar, the market conditions are far from supporting any apprehension as to their immediate future. Both have shown a remarkable capacity for extension without resort to the less remunerative avenues of disposal, and the demand for both seems to be constantly on the increase.

As regards disposal of gas, it is said that the market for fuel and illuminating gas is now fully supplied. But the source of this supply is based on the constant consumption of coal or petroleum oil, barring the cases where natural gas is used. Therefore the question of supply rests on a constant outlay for raw materials. If a supply of completely or partially manufactured gas of higher quality can be offered to the gas companies at the same cost, or an equally good quality at a lower net cost than the existing method of raw material supply and manufacture comes to, they will inevitably turn to the new and more economical source. It is merely a matter of dollars and cents. And that these arguments are worthy of consideration and that such conditions can and do prevail, is attested to by the fact that a considerable number of American cities are now successfully using the gas from by-product coke ovens for all or a large part of their illuminating and fuel requirements. The fact that in nearly every case a continual increase in the gas consumption has made frequent extensions of the gas-making plant necessary, and that the lowering of the price of gas extends its use enormously, must also be given due consideration. There are few American cities that do not anticipate larger gas plants, lower gas prices and greater consumption in the near future.

For these reasons it does not appear to the writer that the immediate extension of the by-product coke oven industry will be fraught with disaster to the by-product markets. In the light of what has gone before, the future does not seem otherwise than most promising.

C. G. ATWATER.



## REVIEWS.

### RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.<sup>1</sup>

BY JOHN D. PENNOCK.

Received July 9, 1906.

IN his address delivered before the Congress of Applied Chemistry, held in Berlin in 1903, Mr. Ernest Solvay drew a striking picture of the fall of the LeBlanc soda process before the more economical ammonia soda process, showing year by year from 1870 to the present the constant lessening of one and the constant progression of the other, until in 1903 the world's production by the ammonia soda process was 1,610,000 tons, and 150,000 tons by the LeBlanc, while in 1873, twenty years before, there were produced by the LeBlanc process 447,000 tons, and only 2,600 tons represented the yearly production of ammonia soda.

Though the production of soda ash was then greatly curtailed, the LeBlanc works by no means had to close their doors, for while by the ammonia process, soda ash could be produced at a much less cost than by the LeBlanc process, there was not so great a difference in the cost of caustic soda as made by the two processes, and while the chlorine, combined with the sodium, the fundamental reagent in both processes, appeared in the LeBlanc process as a decidedly valuable by-product in the form of bleaching-powder, in the ammonia process it appears as calcium chloride, a practically waste product.

Naturally there are many uses to which calcium chloride may be put and for which a small financial return may be obtained, such as a drying agent for air, for refrigerating purposes in the place of brine, for cooking solution in the canning industry, for wall plaster in the Cappon process, and the seasoning of Portland cement, etc., but the sum of all these uses amounts to but a very small percentage of the total calcium chloride produced.

Therefore the mainstay, the prop that has kept the LeBlanc works from utter ruin, is the by-product chlorine, available and salable at a good price in the form of hydrochloric acid or bleaching-powder.

While the ammonia soda process has completely captured the soda ash market, it was expected that electrolytic methods would soon take possession of the bleach market. This assumption was not immediately realized; it required the expenditure of much capital and the failure of many companies before success was achieved, and only within the last year or two could it with certainty be said that electrolytic caustic soda and bleach have been established for all time. But the returns for last year's business indicate that there are at least two factories in England

<sup>1</sup> Read at the Ithaca Meeting of the American Chemical Society.

making a profit, namely, the Castner Kellner Alkali Co. (mercury process), which showed a profit of \$250,000 for 1905, and the Electrolytic Alkali Co. (diaphragm process), which claimed a profit of \$30,000. While the success of these two companies proves that electrolysis of sodium chloride is commercially profitable, the comparison of the returns of these two processes is also indicative of the superiority of the mercury process over the diaphragm process. This superiority is likewise shown in Europe and in the United States.

Hasenclever, at the head of the LeBlanc process in Germany, takes a pessimistic view of the future of the LeBlanc soda industry. He claims one-half the world's production of bleach, 260,000 tons, is made by electrolytic processes.

	Electrolytic Per cent.	LeBlanc. Per cent.
Germany produces bleach.....	65	35
England.....	18	82
France.....	19	81
United States... ..	100	0
Austria.. ..	66	34

Hasenclever says the only hope of the LeBlanc process lies in the discovery of new uses for sulphate and on the growth of the new sulphur dye industry.

Kershaw, on the other hand, when he studied the financial return of \$1,500,000 made by the United Alkali Co., of England, for 1905, puts a more rosy aspect on the future of the LeBlanc works, but he must remember that the profits of this company came not so much from soda ash, caustic and bleach as from the various other chemicals which they produce in addition to the regular products. He too, like Hasenclever, concludes that while there will be some business in soda ash and bleach, their chief profits will come from the manufacture of sulphuric acid, sodium sulphate, hyposulphite, sulphite and other sulphur salts which cannot be made by the processes of either of their rivals.

That but meagre profits are on the whole being obtained in electrolytic soda operations is indicated by the recent tendency the world over to divert the chlorine from bleach into various other lines where better prices may be obtained, such as tin crystals, pure hydrochloric acid by combustion of the chlorine and hydrogen, carbon tetrachloride, and mono- and dichlorobenzene.

The world is in search of a solvent that is cheap and at the same time non-inflammable for use in paints, rubber manufacture, wool washing, etc. Carbon tetrachloride possesses the necessary properties and consequently many investigators are at work endeavoring to devise some cheap method for producing it.

As carbon tetrachloride contains 92 per cent. of chlorine and chlorine can not be made at less than 2 cents per pound, the chlorine alone will bring the cost of carbon tetrachloride to at

least 30 cents per gallon, while the cost of the operation will be as much more.

By the Taylor electric furnace, carbon disulphide may be made in large quantities very cheaply, and with this by the old process, carbon tetrachloride may be more cheaply made than formerly.

Another outlet for electrolytic chlorine is monochlorbenzene, which is a good solvent, having a freezing-point of  $-45^{\circ}$ , boiling-point of  $132^{\circ}$ , and sp. gr. of 1.1125, and which may readily be formed according to Beilstein by passing chlorine into benzene heated to  $50-60^{\circ}$  in the presence of aluminium chloride as a catalyzer.

L. E. Andes (*Chem. Ztg. March*, 1906), on studying the properties of mono- and dichlorbenzene, finds them to have very desirable properties as solvents. Dichlorbenzene distils at  $173^{\circ}$ ; it leaves, on evaporation, no odor or residue. One hundred grams each of monochlorbenzene, dichlorbenzene and turpentine were exposed to the air for fifty hours; 14 grams of dichlor-, 80 grams of monochlorbenzene and 32 grams of turpentine had evaporated. Both mono- and dichlorbenzene can be mixed in all proportions with drying oils, and can often replace turpentine.

Carbonate saponification of fatty acids instead of caustic treatment of neutral fats is meeting with considerable favor in Europe and is quite extensively used, whereas in the United States, thus far, but little progress has been made in that line. It is undoubtedly destined some time to reduce very largely the use of caustic soda for soap-making. One inventor has recently suggested using the crude bicarbonate from the ammonia soda process before drying, but it would appear rather impracticable on account of the ammonia present in the bicarbonate, as it would require condensing apparatus to prevent ammonia loss, which the soap-maker would hardly like to undertake. But carbonate saponification has advantages, chief among them the following:

First, the glycerol need not be dragged through the entire process of boiling as in the saponification of neutral fats. Second, the yield of glycerol is larger. Third, saponification by carbonates is cheaper, as the price of carbonate of soda is much less than that of caustic soda. So far as the process of saponification is concerned, it is immaterial whether the fatty acids employed are obtained by the use of the autoclave, by high or by low pressure, or by the open-kettle methods, such as the sulphuric acid process, the Twitchell process, the fermentative fat-splitting process, or Krebitz', a lime method. The main point is that the fatty acids shall be pure and of high percentage.

The Frasch nickel ammonia process for the manufacture of caustic soda would parallel the ammonia process for carbonate of soda, but in addition to the expensive reagent ammonia, nickel is also required.

By this process nickel hydroxide is added to a saturated solution of ammonia and brine and upon agitation a nickel ammonium chloride separates out and the caustic soda is formed in solution. The double salt, after filtration, is treated with lime, the ammonia evolved and the nickel precipitated in the form of hydroxide ready for use again.

The enzymic fermentation process for the production of fatty acids, due to the work of W. Coustin and his co-workers, as carried out in a working trial in Berlin, has proved a success. The enzyme of the castor oil seed has proved most active. A mixture of 50 pounds cotton oil, 34.5 pounds castor oil seeds, 3.3 pounds water and 2.5 pounds acetic acid, at a temperature between  $70^{\circ}$  and  $104^{\circ}$ , showed after three hours 42 per cent., and in twenty-four hours 90 per cent. of fatty acids. This ready elimination of fatty acids and separation of glycerol combined with saponification with carbonates is of great importance to the soap industry.

By-product coke ovens thus far have been built horizontally, but the process of G. J. Arts, recently patented, makes use of a vertical retort. The retort is cylindrical and the heating flues encircle the retort spirally. The coal is charged in at the top and discharged continually, dropping at the bottom into a closed boiler containing water for quenching. A higher yield of by-products and a higher illuminating value for the gas is claimed for the process since the ascending gases pass through a continually cooling zone, whereas in the horizontal by-product oven the gas carrying its benzene illuminants and ammonia passes over a hot bed of coke at about  $1000^{\circ}$ , where a certain amount of the ammonia is decomposed and where benzene is broken down into naphthalene. Another important point claimed for the process is that the steam evolved from incandescent coke rising through the mass further reduces the sulphur and phosphorus in the coke and at the same time produces a certain amount of water-gas. (*J. Gas Lighting*, May 22, 1906, pp. 519.)

All England is greatly agitated at the present time over the smoke nuisance; the bringing of the offending industrial operator to the court of justice is a daily occurrence in the manufacturing districts.

The rapid development of the coke oven, the Mond and the Loomis-Pettibone producers supplying gas for gas engines and as a cheap domestic fuel, will in the future do much toward reducing the uneconomical and smoke-producing process of direct combustion fuel.

Over 150,000 boiler horse-power capacity of Loomis-Pettibone plants in connection with gas engines have been installed and are now in operation in this and foreign countries.

It is interesting to note that the Union Carbide Co., which thus far has had an entire monopoly in the carbide business, is likely to have a competitor in the Hartenstein process which is in

operation at Constantia, Michigan. By this process carbolite, the name given to the carbide of a stone or flint-like structure, is obtained, which is not objectionably porous, not so hygroscopic and does not yield the percentage of fines that the present carbide does.

The recent activity in the utilization of peat in this country has demonstrated that the briquetting of peat for fuel purposes cannot be economically done. The conversion of peat into gas in producers, and using the gas for power in gas engines, promises to be successful. Certain grades of peat are making a cheap quality of paper. At Capac, Michigan, with a plant working the patented process of C. Esser (Patents No. 690,363, December 31, 1901, and No. 771,202, September 27, 1904) satisfactory results are obtained.

Ethyl alcohol to be used in the arts may be obtained free from tax after January 1, 1907, and it will be necessary to use some sort of a denaturator. In Germany (Fifth International Congress für Angewandte Chemie, Vol. II, p. 560) denatured alcohol is classed as "complete" or "incomplete." To produce "complete" denaturation 2.5 per cent. of a solution made by 4 liters of wood alcohol and 1 liter of pyridine is added to 100 liters of alcohol. "Incomplete" denaturation is the treating of the alcohol for a certain specific use, for instance, alcohol for use in rubber goods, is treated with shellac; for celluloid with camphor, etc.

France uses wood alcohol which must contain 25 per cent. acetone and 2.5 per cent. of empyreumatic compounds. Also heavy benzene, 150° to 200°, and other substances for special purposes.

Austria uses the same denaturators as Germany.

Switzerland uses 2.9 per cent. of a solution made up of 70 per cent. acetone, 10 per cent. pyridine, 10 per cent. solvent naphtha and 10 per cent. of the last runnings of wood alcohol distillation.

The few chemical processes and problems which my limited time has permitted me to touch upon thus far dwindle into insignificance when compared with that subject which of late has occupied the attention of many investigators; namely, the "fixation of nitrogen" in a form suitable for fertilization of vegetable growths. One can with difficulty name a subject of greater importance for future generations of mankind as well as our own than that which has to do with the supplying of food for the rapidly increasing population of the world. Any process for the production of nitrogenous substances convertible into vegetable tissue when mixed with the soil, should be hailed with delight. The cost of manufacture by such a process may at the present be so great as to preclude operating in competition with the present sources of supply, but the time will certainly come, if the process is technically possible, when conditions will so change

that the costly process of to-day will be the cheap process of to-morrow. Many of the important industrial operations of to-day, founded on reactions discovered generations ago, were successfully established only after sufficient advance in engineering and the arts in general made them possible. The reaction often remains dormant until the accumulated thought and experience of patient investigators, who perhaps have failed, but nevertheless have added one link in the chain of experience, ultimately brings commercial success. Humphry Davy, seventy-five years ago, demonstrated the results of electrolysis of sodium chloride, but it was many years before the dynamo made it commercially profitable.

The rise of the ammonia soda process offers another example. The basal reaction of the process was placed by Fresnel in competition with LeBlanc's before the French Tribunal, but was rejected because at that time no method for the recovery of ammonia was known. From that time until 1863 a dozen or more investigators tried to produce a commercial process but failed, but by each succeeding failure knowledge was gained, which ultimately brought success in the Solvay process.

In creating luxuriant vegetable growths by fertilization it is impossible to say which of the constituents in a fertilizer is the most important, phosphoric acid, potassium or nitrogen. All three are perhaps equally important and at the present time available in large quantities, and for many years to come the extended areas of potash salts in Germany, and the recently discovered salts of France, will furnish the supply of potassium, and when these are consumed a process for the separation of potassium from feldspar will furnish the requirements of plant life for years after the Stassfurt or similar deposits have been exhausted. Search for potassium deposits in this country should not be abandoned. Though the Michigan company which put down a well in Wyoming in 1899 in search of potassium salts failed, further trials should be made; rather the government should drill wells, and if successful, obtain a rental of the mines as the German government is now endeavoring to do. Mr. Courtis (*Min. Ind.* 1904) claims the locations favorable for the discovery of potash salts are (1) Cady, Wyoming; (2) Magnesium Lake, Laramie Co., Wyoming; (3) Brown Springs, Cal.; (4) Death Valley, Cal.; (5) Bound Brook, N. J.; (6) Mt. Tom, Mass.

The fact that the waters of many of the alkali lakes contain 8 to 10 grams per liter of potassium chloride may indicate a deposit of soluble salts or the decomposition of insoluble silicates.

The United States, which imported from Germany 216,000,000 pounds potash in 1905, valued at \$3,551,000, should sometime have its own source of supply; for the Kingdom of Prussia, which is endeavoring to secure control of the potash salt mines, and has recently offered \$7,000,000 for one of the large mines,

will doubtless curtail the exportation and advance the price of the exported product to enable its own farmers to use larger quantities at lower prices.

No better service could be done by Congress for the good of the agricultural interests than to appropriate \$1,000,000 for the prospecting of potash salts, which are undoubtedly to be found somewhere within the boundary of the United States. There is no chemical investigation whose successful operation would bring greater financial returns than the separation of potassium from the potash feldspars which are to be found in large quantities in this country.

As for phosphoric acid, the United States has an abundant supply in the deposits of rock phosphate of the Southern States, and in apatite, which is found in many places in considerable quantities.

But as to the supply of nitrogen we are not so fortunate. The syndicate formed for prospecting in the Western States for nitrates thus far has produced no appreciable amount. The deposits on the western coast of South America will be depleted before many years, possibly within 30, and the great nitrate combine, recently formed, is continually advancing prices, and before another generation has passed we shall have to resort to some other source of nitrogen for the soil.

Briefly referring to nature's methods of securing available nitrogen, we first note that electric discharges during storms undoubtedly form oxides of nitrogen which are carried to the soil by rain and combine with alkalis in the earth to form nitrates.

Another of nature's processes of nitrogen fixation is that discovered by a German farmer, Schultz, who observed that certain plants, clover, peas, lentils, etc., greedily absorb nitrogen, and accordingly initiated the practice of turning under the early crops of these products to furnish nitrogen for the following crops. The reason for the lentil's power to thus fix nitrogen was later, in 1874, found to be due to tubercles produced on the roots of the plant by microorganisms. Other plants do not have these tubercles and hence cannot assimilate nitrogen to the same extent. That the fixation of nitrogen is thus going on is acknowledged by all biologists.

The efficacy of barnyard manures, tankage, garbage and other highly nitrogenous fertilizers is due to the ready formation of ammonia through the influence of bacteria in the soil.

It is unnecessary in this connection to dwell upon the work of these microscopic agencies, one class of which, called the ammonifiers, breaks down the organic substance forming ammonia, which is eagerly seized by the nitrifiers, producing a synthetic reaction and forming with oxygen nitric acid which is immediately taken up by an alkali forming a nitrate, in which form it is readily assimilated by the plant.

But we will pass over these natural methods and take up the application of natural inorganic and artificially produced nitrogenous substances.

In the first class we have sodium nitrate at present found in only one part of the world, Chili, and produced by a process of leaching and purification, the entire output being controlled by the nitrate kings of England.

The production of this mineral is rapidly growing and it is expected that before many years the supply will be exhausted; for not only is the demand for it as a fertilizer increasing, but the production of nitric acid is constantly increasing, causing an additional drain upon the supply.

In the year 1905 the production of sodium nitrate amounted to 1,733,644 tons, three-quarters of which was used in fertilizers.

	1904. Tons	1905. Tons.
Production of sodium nitrate.....	1,540,000	1,733,644
Shipments of sodium nitrate to Europe..	1,179,500	1,192,120
Shipments of sodium nitrate to United States.....	265,766	353,177
Shipments of sodium nitrate to other countries...	35,042	52,605

We come now to the artificial production of nitrogen-bearing salts suitable for stimulating the growth of vegetation and will first consider those schemes for the direct fixation of the nitrogen of the air by which the nitrogenous fertilizers of the distant future will undoubtedly be supplied, and leave for later consideration the form of nitrogen salts, namely, sulphate of ammonia, the result of the dry distillation of organic substances; for undoubtedly the importance of ammonium sulphate as a fertilizer will greatly increase in the near future, gradually supplanting the waning supply of nitrates, and by reason of its much cheaper production postpone indefinitely the commercial fixation of nitrogen by electricity.

There is to-day no subject of chemical investigation of more vital importance than the fixation of nitrogen. It has already been accomplished on a small commercial scale by two different methods, but at a cost which probably is not sufficiently low to permit of successful competition with the present supply of nitrogen for fertilizer purposes, or for the manufacture of nitric acid. It was early determined by Wöhler and Deville that elementary silicon in contact with nitrogen resulted in a combination. Later it was found that boron, silicon, magnesium and titanium readily formed nitrides (convertible to ammonia with water) in an electrical furnace in an atmosphere of elementary nitrogen. Kaiser alternately leads nitrogen and hydrogen over magnesium hydride, producing ammonia, by the following reaction:

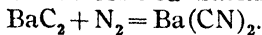


The commercial results of the experiments in these lines have been unsatisfactory.

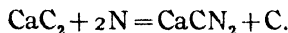


As is well-known, the only processes which have attained results approaching success, are Dr. Frank's calcium cyanamide process, and Birkeland and Eyde's process of fixation by electric discharge.

In 1903, while in Berlin, at Siemen & Halske's laboratory, it was my good fortune to see Dr. Frank's apparatus and the various products which were the result of his first work in fixation of nitrogen, calcium cyanamide, dicyanamide, etc. From that time cyanamide experimentation has continued and the beneficial effect of calcium cyanamide as a fertilizer thoroughly demonstrated; while a considerable quantity has been produced a careful study of the process would show that as at present operated calcium cyanamide could hardly be produced in competition with nitrate or ammonium sulphate. Dr. Frank's first observation, greatly to his surprise, was that when using calcium carbide and nitrogen at high temperature he got calcium cyanamide instead of calcium cyanide as he had expected from his experiments with barium carbide in which he formed barium cyanide.



With calcium carbide half the carbon was given off and he got calcium cyanamide.



Instead of first making carbide and passing nitrogen over calcium carbide at 900–1000°, the regular carbide process may be carried on in the presence of nitrogen and calcium cyanamide results. The most costly part of the process is the necessity of using nitrogen from which oxygen has been removed. This can be done only at considerable expense, either by passing over copper, or taking it from liquid air.

In arriving at a cost of calcium cyanamide which contains 16.5 per cent. available nitrogen, one must start with the cost of calcium carbide which at \$20 per horse-power year is stated to be from \$25 to \$30 per ton. To this must be added the cost of the preparation of nitrogen free from oxygen and due allowance must be made for leakage and loss of this costly nitrogen. When all expense is carefully summed up, it is quite certain the cost per unit of nitrogen in cyanamide will be in excess of the cost of nitrogen in sulphate or nitrate.

In an address before the Chemical Congress recently held at Rome, Dr. Frank stated that while one electrical horse-power year would produce the necessary carbide for the binding of 772 kilos nitrogen, still in practice only about 300 kilos were fixed as cyanamide. He reiterates the necessity for cheap electrical power and refers to the Linde process for obtaining his liquid air and further suggests that, as by action of steam at high pressure on cyanamide he obtains ammonia, he can use the oxygen of the liquid air for oxidizing the ammonia to nitric acid, thereby obtaining this product more cheaply than by the Birke-

land and Eyde process. It has also been suggested that as the fixation of nitrogen proceeds more rapidly with an excess of oxygen in the air, the cyanamide and the Birkeland and Eyde process might be located together, the former taking the nitrogen, and the latter the oxygen of Linde's liquid air.

Other chemicals of much interest have been developed out of the experiments with calcium cyanamide which will doubtless be of considerable commercial value, namely, calcium dicyanamide, dicyandiamide, guanidine and its salts.

In a letter recently received from Dr. Frank he states that a separate company has been formed for the manufacture of calcium cyanamide derivatives, and that dicyandiamide will be on the market for use in explosives and for the hardening of steel.

It is nothing new to attempt the combination of nitrogen and oxygen to form nitric acid. Over 120 years ago Cavendish observed under influence of the electrical discharge the formation of oxides of nitrogen. Since 1893 this problem has again been vigorously attacked by Crookes, Lord Rayleigh, Nernst and others in the laboratory, and by the Atmospheric Products Co., of Niagara Falls, Kowalski in Switzerland, and Birkeland and Eyde in Norway, on a commercial scale. As is well known, the only method to achieve any considerable success is that of Birkeland and Eyde.

Dr. Otto N. Witt describes a visit to the Norwegian plant at Nottoden (*Chem. Ind.*, December 1st), and says the essential feature is that an electric arc is made to continually alter its path by the alternations of a powerful magnet. The gases from the furnace, containing only 2 per cent. nitrous gas, are very hot and must be cooled before going to the absorbing apparatus which is the same as in nitric acid works. A strength of acid equal to 50 per cent. is obtained. The heat of the gases leaving the furnace is utilized in making steam under boilers and in evaporating the solution of calcium nitrate. The weak gases are absorbed in towers of granite down which milk of lime passes.

According to Dr. Witt the Norwegian plant produces 1.5 tons daily and he states the yield to be 455 kg. 100 per cent  $\text{HNO}_3$  (592 Kos.  $\text{Ca}(\text{NO}_3)_2$ ) per kilowatt year, which he figures at the ridiculously low price of \$4.00, whereas \$16.00 would be more nearly the cost of power. Guye claims the yield per kilowatt year to be 500 kg. and the *Chemical News*, 650.

At a recent conference (*L'Echo des Mines et de la Métallurgie* 33, 1776, March, 1906, p. 379) of scientific and business men called together by M. L. Grandeau, chief of the French agricultural stations, Mr. Eyde was present and stated that since May 2, 1905, three furnaces of 500 kilowatts had been in run, each using 25 cubic meters of air per minute and that their calcium nitrate product contained 13 per cent. nitrogen and he gave 112 fr. (\$22) as the cost of the power per ton of nitrate, assuming 15

fr. or \$3 as the cost of a horse-power, absurdly low. If we assume the cost of power, \$18, as attainable at Niagara Falls, the cost for power alone per kilo ton of calcium nitrate would be \$132, containing 13 per cent. available nitrogen, as against \$52 per ton for sodium nitrate containing 15 to 16 per cent. nitrogen, and \$60 for ammonium sulphate, containing 21 per cent. nitrogen. Thus, unless electrical power can be obtained for \$5 or \$6 per horse-power year calcium nitrate cannot compete with ammonium sulphate as a fertilizer.

While the cyanamide at no very distant day may be produced commercially at such few places as can furnish power cheaply, the direct oxidation of the nitrogen of air by electric discharge I consider to be a problem far from being satisfactorily solved. It is endothermic, requiring 3.7 times the power that the exothermic cyanamide process does.

The suitability of calcium nitrate for fertilizer purposes is yet untried. Calcium cyanamide, on the other hand, has been thoroughly tested by many investigators and has been found to correspond closely in value to sodium nitrate and ammonium sulphate. L. Grandeau (*J. Agr. Prat.* No. 1, pp. 8-10 (1906)), in experiments with potatoes, showed the relative effectiveness of the three fertilizers to be sodium nitrate 100, ammonium sulphate 96.5, and calcium cyanamide 93.4.

While the cyanamide process or the nitric acid process may at some quite distant date be made commercially economical, yet the immediate supply of suitable nitrogen compounds to take the place of sodium nitrate is ammonium sulphate made first and in greatest quantity by gas houses and by by-product coke ovens, second by Mond producers, third, from the destructive distillation of peat and garbage.

The relative importance of sodium nitrate and ammonium sulphate to the fertilizer industry is shown by a comparison of the figures representing the production of the two salts. In 1905, the production of sodium nitrate amounted to 1,733,000 tons, of which 1,290,000 reached the soil as fertilizer, while the production of ammonia, figured as sulphate, of Great Britain, France, Belgium, Germany, Italy, Austria, Spain and the United States amounted to 557,000 tons, of which about 80 per cent. or 445,000 tons was used in fertilizers.

It is interesting to note that of the production of 557,000 tons of ammonium sulphate per annum, 44 per cent. was produced by Great Britain, 20 per cent. by Germany, 12 per cent. by the United States and 9 per cent. by France.

Another matter of interest is that of this 244,000 tons of ammonium sulphate produced in Great Britain per annum, 60 per cent. comes from gas works, 7 per cent. from blast-furnaces, 15 per cent. from shale plants, 10 per cent. from coke ovens, and 5 per cent. from Mond gas producers.

## WORLD'S PRODUCTION OF AMMONIUM SULPHATE FOR 1905.

	Tons.
Great Britain.....	244,000
France.....	43,000
Belgium.....	39,000
Germany.....	115,000
Italy, Austria and Spain.....	48,000
United States.....	68,000

Great Britain's ammonium sulphate came from the following sources:

	1902 Tons.	1903 Tons.	1904. Tons.
Gas works.....	150,055	149,489	150,208
Blast-furnaces.....	18,801	19,199	19,568
Shale plants.....	36,931	37,352	42,486
Coke ovens.....	15,352	17,438	20,843
Gas producers.....	8,177	10,260	12,880

France's ammonium sulphate comes from:

	Tons.
Paris gas works.....	12,000
Provincial gas works.....	6,000
Paris sewage works.....	7,600
Provincial sewage works.....	3,500
Coke ovens.....	12,900
Shale.....	1,000

By what follows I hope to show that through the rapid extension of by-product coke ovens and the permanence of the industry, the waning supply of nitrogen due to the depletion of the nitrate deposits will be made good by ammonium sulphate, which is produced at the rate of 17 to 26 pounds for every ton of coal coked.

As long as coal lasts there will be a continually increasing production of ammonium sulphate. Foundries are located in large cities, blast-furnaces too are being constructed more and more in the neighborhood of cities which are not too far from the ore beds. Coke ovens will follow the blast-furnaces and in such location on the border of a large city the by-product coke oven can perform to the fullest extent its various functions.

A moment's consideration of the by-product coke oven and what it accomplishes will convince one that it is the foundation of an industry, now in its infancy, but destined to be chemically and metallurgically one of the most important and far-reaching industries in the domain of arts.

Its permanence as a source of nitrogen in a cheap form for fertilizer is assured by its underlying and fundamental importance in the operation of various industries. By it better coke, both for blast and foundry purposes, is produced than in bee-hive ovens. This is freely acknowledged by the best engineers in the country. A better price can be obtained from the foundrymen for by-product coke than for Connellsville because of its superior physical quality. This alone would insure the permanence of the

industry. But further, by it a superior quality of tar, the starting point for various industries rapidly becoming of importance, is produced in quantity varying from 60 to 100 pounds per ton of coal. The saturation of paper and felt with tar for roofing purposes is an industry of considerable importance. As a fuel in combustion engines by-product tar may be used as successfully as petroleum oil. Upon the products of the distillation of tar various industries are dependent. The utilization of pitch in the manufacture of briquettes is comparatively a new one in this country, but is destined to become of great importance, particularly to work up into valuable form the anthracite culm piles of Pennsylvania and the breeze of coke plants. Plants have recently been installed in Scranton, Detroit and Montreal for the manufacture of briquettes. Tar macadam roads, made with regular macadam foundation and an upper layer of three inches of a mixture of fine spawls and a certain grade of pitch, make a pavement perfectly impervious to moisture.

The distillate from tar has many uses, the most common being for the well-known purpose of creosoting railroad ties. Railroad men are convinced from long-continued experience that no other method of treating ties to preserve them is as satisfactory as creosoting with coal tar distillate which must have a high content of naphthalene. Large quantities are used for making lamp-black. As the consumption of pitch for briquetting purposes increases, which requires the distillation at a high temperature, anthracene will be produced in large quantities and will be shipped to Europe for alizarine manufacture, and let us hope to find a market in this country for the same purpose.

One branch of the by-product coke industry thus far very little developed, but destined to be at some future time of immense importance, is the recovery of the aromatic oils of the gas.

Of the 10,000 cu. ft. of gas produced from a ton of coal, 6,500 cu. ft. are required in the coking process. This gas contains on an average 0.75 per cent. benzene and its homologues. Now the heat value of this gas is affected only slightly by the removal of benzene. By washing gas with petroleum or coal tar oil, a benzolized oil containing 2 to 3 per cent. of benzene is produced and by distillation a crude benzene light oil is obtained.

Only slight quantities of impurities, carbon disulphide, hydrogen sulphide, thiophene and naphthalene are found to be present, and purification and redistillation furnish a benzene 100 per cent. pure and suitable for nitrifying and converting to aniline.

What does this signify—what potentiality is here contained? The raw materials for all the aniline colors now imported into the United States are valued at millions of dollars. Formerly, it it could be said that the raw materials for a color industry were lacking in this country. This is no longer true. An abundance

of benzene is now available. How long before some enterprising company will take the initiative and on a considerable scale will undertake the manufacture of colors. As deterrents against the investment of capital in the color industry are offered on every hand: (1) lack in this country of competent chemists at low salaries, and (2) high price for labor, (3) the strong entrenchment of the business in the hands of the Germans, a business for which they have been peculiarly endowed. The close co-operation of the German teachers in chemistry with the manufacturer was admitted by Ostwald in an address while in this country to be the reason for Germany's control of the color industry. Our scientific schools are turning out chemists in large numbers and no one of our teachers is willing to admit they are not as well trained as the German chemists. The superior ingenuity of the American would soon devise machinery to displace labor; the raw materials, alkali and benzene, may be obtained at a lower price in this country than in Germany; nitric and sulphuric acids can be made as cheaply here as in Europe. There is no question but that under these conditions the aniline color industry, established with ample resources, after four or five years would return ample profits to the capital invested.

It is now about ten years since Mr. Fulton's comparison of Connellsville and Semet-Solvay coke in the Buffalo blast-furnaces dispelled all fears in the minds of metallurgists as to the suitability of by-product coke. Sir Lowthian Bell's statement of the loss of carbon in the upper part of the furnace was disproved.

A similar distrust came to gas manufacturers when it was suggested to them that by the coke oven equally good gas could be produced as by the gas retort. The recent installation of 120 ovens at Chicago, now supplying 3,000,000 cu. ft. of high candle-power gas to that city, in addition to plants of equal size at Milwaukee and Detroit, which have been in successful operation for more than two years, have now dispelled all the doubts of gas-makers as to the success of the by-product gas.

There is at present in the United States over 20,000,000 cu. ft. per day of illuminating gas enriched by benzene being furnished by coke ovens. It was supposed that in cold weather and under pressure coke oven gas enriched with benzene would lose much of its candle-power. An elaborate series of experiments on coke oven gas of an initial candle-power of 13 candles showed that this gas could be enriched to 24 candle-power and stand a temperature of zero, and a pressure of 20 pounds without appreciable loss. The experiments correspond closely to what calculations by vapor-pressure showed to be expected.

When one considers the operation of the coke oven when run as a producer of illuminating gas it is evident at once that it should produce gas superior to the ordinary coal gas made in the small gas retort. In the first place the higher temperature of the gas

retort tends to break down the illuminating series, benzene, into naphthalene. In the distillation of coal the gas richest in lighting properties is evolved during the early part of the process, the gas during the later period of distillation being poor in illuminants. Now all the gas from the gas retort rich and lean making a low average, is used, whereas in a coke oven only the rich gas, only that evolved during the first six hours, or one-fourth of the distillation period, is used for illuminating purposes, while the balance after giving up its benzene to the rich gas of the first six hours to make it richer, goes back to the ovens to effect the coking of the coal. It has been proved that gas of 15 to 16 candle-power can be made from coals not considered gas coals and of very low volatile matter by this selection method, and by addition of the benzene of the lean gas to the rich gas a candle-power of 19 to 20 is obtained.

As before stated, the amount of ammonia recovered varies from 16 to 27 pounds of sulphate per ton of coal, and is directly proportional to the percentage of volatile matter in the coal, a coal of 18 per cent. volatile matter yielding 16 pounds of sulphate, and one of 37 per cent. yielding 27 pounds. But this is a small percentage of the theoretical yield from the nitrogen of the coal. If all the nitrogen were converted to ammonia and recovered as such, the yield would be 133 pounds. But we find in the coke 48 per cent. of the original nitrogen.

While experimenting with certain Illinois coals it was found that the yield of ammonia was exceptionally high, and it was accounted for by the fact that the coal contained from 2 to 3 per cent. calcium carbonate. Lime will increase the yield of ammonia 20 to 40 per cent.

While a certain coal under one form of treatment, for instance, in the coke oven, yields 24 pounds of ammonium sulphate, the same coal under another treatment in Dr. Mond's producer at lower temperature and with steam returns 75 pounds of ammonium sulphate. The rapid construction of Mond-producer plants, particularly in England, will very largely increase our supply of nitrogen for the soil. Other nitrogenous substances are destined in the near future to add to our supply of ammonia, particularly as straight distillation results in such a large yield. I refer to the distillation of peat and to the distillation of garbage and other organic refuse. Peat in dry distillation yields 40 pounds, garbage 79 pounds of ammonium sulphate to the ton.

To recapitulate, we have as features of the by-product coke oven, which have been shown to be important as working toward its permanence and consequently as furnishing a permanent source of fertilizing nitrogen; (1) the production of coke superior to bee-hive coke; (2) the production of tar which enters so extensively into the arts; (3) it is furnishing the thus far-lacking material, benzene, in large quantities for the establishment of the color industry, but used until the establishment of this industry in

enriching gas for illuminating purposes; (4) it produces illuminating gas at a lower cost and of superior quality to that made in a gas retort; (5) it furnishes cyanogen equivalent to  $1\frac{1}{2}$  pounds of potassium ferrocyanide per ton of coal; (6) as one of the by-products, it supplies the pyridine soon to be in demand for denaturing alcohol; (7) the hydrogen sulphide recoverable from the ammonia liquors when oxidized is sufficient to supply nearly one-half the sulphuric acid required in converting the ammonia into sulphate.

Therefore, let those take courage who have been predicting universal famine from lack of fertilizer nitrogen when the nitrate deposits shall be exhausted, for as long as our mines yield bituminous coal, by-product coke ovens will produce an ever-increasing amount of ammonia. As long as carbon in any form may be obtained, calcium cyanamide will carry nitrogen to the soil, and even after all carbon has been consumed, if only the rain continues to fall and rivers to produce water-power and hills give forth their limestone, and the earth is enshrouded with its nitrogenous atmospheric mantle, basic calcium nitrate, by the Birkeland process, will furnish the languishing vegetation with its necessary nitrogen.

SOLVAY PROCESS CO.,  
SYRACUSE, N. Y.

## A REVIEW OF THE AMERICAN PORTLAND CEMENT INDUSTRY.

BY RICHARD K. MEADE.

Received July 9, 1906.

Now that the United States ranks first of the Portland cement producing countries of the world, not only in point of the quantity manufactured but also with regard to quality, it seems fitting to take a look backward at the industry and see by what steps this success has been gained. First the enormous amount of engineering work now being done in this country has created a steady demand for Portland cement; second, the cheapening of the process of manufacture has allowed it to displace to a large extent other hydraulic cements, and also wood, stone and brick; third, the introduction of reinforced concrete, concrete building blocks, sewer pipes, etc., has widened enormously the field of concrete construction. All these causes have contributed to the wonderful growth of the Portland cement industry.

Few people realize how much concrete construction is done in the United States. If all the Portland cement made in this country last year had been used for sidewalks, these would have been equivalent to a sidewalk over 16 feet wide, reaching entirely around the world, at the equator. If this same cement



had been made into a solid cube of concrete, an edge of this would be three-sixteenths of a mile in length.

At the present time the Portland cement industry in America ranks second of the non-metallic industries in point of value, being exceeded only by the production of coal, oil and natural gas. It is entirely dependent upon the chemical profession for its existence and, indeed, gives employment to about 250 chemists.

At the present time there are approximately 90 Portland cement works in actual operation. According to the United States Geological Survey, these produced in 1905, 35,246,812 barrels of cement valued at \$33,245,867. The enormous and rapid growth of the industry is shown by the fact that in 1880 only 42,000 barrels of cement were manufactured in this country, while last year's production was over 839 times this amount. The first Portland cement plant produced only 1,700 barrels a year, while one large modern cement plant claims a capacity of more than ten times this quantity daily.

The American Portland cement industry had its origin about 1874 when three small plants were started; one each in Pennsylvania, Michigan and Indiana. Roman, Rosendale or "Natural" cement had been made in this country since 1828, when cement rock (an argillaceous limestone) was discovered along the line of the Erie canal in New York. All the Portland cement used in this country prior to 1874 came from Europe, and chiefly from Germany and England.

In Pennsylvania, the Coplay Cement Co. was organized in 1866, to manufacture natural or Roman cement at Siegfried, Northampton Co. A few years later the manager of this company, Mr. David Saylor, as the result of experiments, became convinced that Portland cement could be manufactured from the rocks of his quarry, and after many trials and some failures and discouragements his company began the manufacture of Portland cement in 1875, and has been a continuous producer ever since. About 1871 Mr. Thomas Millen and his son, Duane Millen, began manufacturing cement sewer pipe at South Bend, Indiana, importing English Portland cement for the purpose. Their attention was called to the probability of manufacturing Portland cement from the marls and clays found around South Bend by a former employee of the English firm of Portland cement manufacturers, Knight, Bevan and Sturge, of Northfleet. They, thereupon, began investigations which led them to establish a plant at South Bend sometime about 1875. In 1872 a small plant, called the Eagle Portland Cement Co., was started at Kalamazoo, Mich., by Chicago capitalists. Plants were also built at Wampum, Pa., at Rockport, Me., and in the Rosendale District of New York, prior to 1880. Of these three plants, however, only one, that at Wampum, was at all successful. The Eagle Portland Cement Co. also failed. Of the six plants mentioned only one has achieved

any marked success, namely the Coplay Cement Company, which is now a large manufacturer.

Other Portland cement plants which were established before 1890 are the American at Egypt, Pa. (near the Coplay); the Empire at Warners, Onondaga County, New York; the Buckeye at Harper, Logan County, Ohio; and the Western at Yankton, South Dakota.

Portland cement is now manufactured in this country from the following raw materials—cement rock and limestone, limestone and clay or shale, marl and clay, and limestone and blast-furnace slag. In 1905, 52½ per cent. of the Portland cement manufactured in this country was made from cement rock and limestone, 36½ per cent. from limestone and clay or shale, and 11 per cent. from marl and clay. The manufacture of cement from cement rock and limestone is distinctly an American process, but both limestone and clay, and marl and clay have been used for this purpose abroad.

Cement rock is an argillaceous limestone found in a narrow belt, extending in a northeasterly direction through the counties of Berks, Lehigh and Northampton in Pennsylvania and Warren County in New Jersey. The deposit is about 50 miles long and is nowhere more than four miles wide. Cement rock contains from 65 to 80 per cent. carbonate of lime and from 15 to 25 per cent. silica, oxide of iron and alumina taken together.

The early cement plants using clay and marl or limestone and clay all followed closely the European practice of cement manufacture, which consisted in finely grinding a wet mixture of marl and clay or limestone and clay and then moulding the mixture into bricks, which were burned in some form of upright kiln. Those plants using cement rock and limestone, however, found it impossible to get the fine crystalline mixture to cohere sufficiently to form briquettes which could be handled without crumbling. At the Coplay Cement Co's. plant, therefore, a small percentage of cement was added to the mixture as a binder, while at the American Cement Co's. plant at Egypt, coal tar was used for this purpose. The use of cement rock as a raw material and the employment of coal tar as a binding material constituted the first advancement of American over European practice.

The machinery for grinding both the raw material and the cement clinker at these early cement mills was very primitive. Mill stones, such as are used for grinding flour in the small water-power mills with which we are all familiar, were used to grind both the clinker and the harder raw materials while edge runner mills were used to grind clay and marl. As the output of these early plants increased the need of more efficient grinding machinery also grew, and ball and tube mills were imported from Europe and used for grinding both the clinker and the raw materials. Several distinctly American forms of grinders were also intro-

duced in the early eighties. The Gates gyratory crusher was found to be best suited to the crushing of hard material, such as limestone and cement rock, preparatory to its final reduction by other means. The Griffin mill was introduced into the plant of the American Cement Company at Egypt, Pa., in 1885, and soon became a very popular mill. The Atlas Cement Company about the same time installed a somewhat similar type of pulverizer, the Huntington mill, the use of which never became general, however. Of recent years two new forms of fine grinders have been introduced—the Kent mill and the Fuller Lehigh mill. The Edison Portland Cement Company uses a system of fine grinding peculiar to itself, consisting of rolls followed by air separators, the idea of the well-known American inventor, Thos. A. Edison.

At the present time mill stones have been entirely done away with except at one or two small mills, and practically all the grinding is now done by one of the following systems:

#### FOR GRINDING LIMESTONE AND CEMENT ROCK.

##### I.

- (1) Gates crushers.
- (2) Ball mills or comminuters.
- (3) Tube mills.

##### II.

- (1) Gates crushers.
- (2) Rolls.
- (3) Griffin mills or Lehigh mills.

#### FOR GRINDING PORTLAND CEMENT CLINKER.

##### I.

- (1) Ball mills.
- (2) Tube mills or comminuters.

##### II.

- (1) "Pot" crushers.
- (2) Rolls.
- (3) Griffin mills.

##### III.

- (1) Kent mills followed by air or screen separators.

The cement mills built prior to 1890 all used upright kilns similar to those used abroad. Some of these represented the most improved forms. The Coplay used the Schoefer kiln, the Buckeye employed the Dietsch kiln and the Western installed the Johnston kiln. These kilns were economical with respect to fuel but very costly as regards labor. A rotary kiln had been invented by an English engineer, Ransome, in 1885 but had never been successfully used there. The Atlas Portland Cement Company became interested in this form of kiln and installed it in the plant they built in 1888 at Northampton, Pa. After much experimenting they succeeded in operating this form of kiln successfully. The upright kilns all required the raw materials to be moulded into bricks which were fed into the kiln alternately with layers of coke or other fuel. With the rotary kiln on the other hand the fine material could be fed into the kiln in the form of a powder, thereby saving much labor. The clinker from the upright kilns is also very unevenly burned, necessitating hand-sorting to remove the underburned portions. The clinker from the rotary kiln on the other hand is very uniformly burned and requires no sorting.

The rotary kiln, though an English invention, has been developed and made practical entirely through American brains,

Seaman, Hurry and Navarro being chiefly connected with the making of its success. Shortly after the utility of the rotary kiln upon dry materials had been proved, S. B. Newberry, formerly a professor of chemistry in Cornell University, adapted it to use with wet materials, pumping the mixture of clay and marl, containing 50 to 60 per cent. water, directly into the kiln.

Ransome heated his kiln by means of producer gas, but oil was generally used in this country until about 1899 when burning with powdered coal was introduced. This latter is now generally used for burning, except in sections where oil or natural gas is cheap.

At the present time, practically all the cement manufactured in this country is burned in rotary kilns. They have also been introduced extensively abroad and probably in the next ten years will displace other forms of kilns even in Europe.

As installed up to a few years ago rotary kilns were usually made 60 feet long and 6 feet in diameter. These kilns were found to be wasteful of fuel, as over 45 to 60 per cent. of the fuel energy was lost in the fuel gases and another 10 to 15 per cent. in the hot clinker.

At the present time two methods are being experimented with for the saving of the heat in the kiln gases.

(1) Lengthening the kiln, thereby giving greater time for the material to absorb the heat of the kiln gases.

(2) Passing the gases of the ordinary short kiln through an upright boiler and then through an economizer.

Thomas A. Edison is the chief exponent of the long kiln, as those in his plant at Stewartsville are 150 feet long. These kilns were put in operation in the fall of 1903 and proved entirely practical and effected the economy in fuel which the inventor had promised they would. His experiment was watched with great interest, and, as soon as the success of these mammoth kilns was known, several of the mills, then under construction lengthened their kilns to 80 feet. This plan has also been tried by some of the older mills who extended their kilns to from 100 to 140 feet. Several of the mills now being built are erecting 100, 125 and 140-foot kilns.

The attempt to utilize the heat of the kiln gases under boilers was first made, I believe, at the plant of the Nazareth Portland Cement Co., but after encountering many difficulties, the plan was abandoned and the boilers taken away. Prof. R. C. Carpenter, of Cornell University, however, has successfully tried this plan at the plant of the Cayuga Lake Cement Co., and also at that of Kosmos Portland Cement Company.

A number of devices have been patented, designed to utilize the heat carried off by the clinker. None of them is used to any extent. A rotary cooler below the kiln through which the clinker

passes and through which the air for combustion is drawn by the kiln draft seems the simplest and most feasible device.

The improvement in the quality of cement has been as marked as the improvement in the process of its manufacture. General Gilmore, in a test made of the Eagle Portland cement, in 1876, found its strength to be less than 300 pounds per square inch after seven days, while to-day cements having a seven-day neat strength of 700-800 pounds are the rule and not the exception. Some of this improvement is no doubt due to the increased efficiency of grinding machinery and it is now an easy matter to obtain a cement 95 to 96 per cent. of which will pass a No. 100 test sieve.

American cement technologists have also made some very noteworthy contributions to the scientific literature of cement. Perhaps the most extensive investigations undertaken by an American chemist are those detailed by Mr. Clifford Richardson in his numerous papers on the chemical constitution of Portland cement. His investigations are perhaps the most interesting of any of the numberless attempts to solve the riddle of what is Portland cement and what gives it its binding properties. Another investigation made some ten years ago along the same line was that of Spencer B. and Wm. B. Newberry. Prof. A. V. Bleining has also investigated the composition of Portland cement. While the volume of work done upon this subject in the United States is not as large as that published by German scientists, what has been done here is of probably just as high a grade as that carried out in Europe, in spite of the distinction of some of the foreign investigators. Prof. E. D. Campbell has carefully experimented to find out the influence of the ratio of lime to silicates and also of fine grinding of the raw materials upon the clinkering temperature. Richards, Soper and Carpenter all measured the thermal efficiency of rotary kilns. Richards investigated that of a 60-foot kiln, Soper that of one of 100 feet and Carpenter that of a kiln whose waste gases were used to fire a boiler. W. B. Newberry investigated the regularity of burning a 60-foot kiln and Meade proved the loss of alkalies and sulphur in burning. He also showed the contamination of the cement by the fuel ash to be smaller than it had generally been considered. Carpenter investigated the substitution of calcium chloride for gypsum to retard the setting time of cement and Meade and Gano showed that calcium sulphate in any form could be used for this purpose. In addition to the above more important papers, the technical press has contained frequent articles upon cement manufacture by Newberry, Lathbury, Spackman, Lesley, Carpenter, Eckel, Meade, Lewis and Lundteigen. Three books dealing exclusively with Portland cement manufacture and two others largely devoted to the subject have also been published. Four trade papers are now devoted exclusively to cement

technology and the uses of cement and many valuable papers have been published in these.

On the physical testing of cement the work done in this country has been excellent. In the early eighties the American Society of Civil Engineers appointed a committee to investigate the subject of cement testing. This committee reported in 1885. Later another committee was appointed which reported January 21, 1903. This report was amended January 20, 1904, and the methods of test recommended by it are now considered the standard ones.

The American Society for Testing Materials turned its attention to the drafting of uniform specifications for cement and its committee reported June 17, 1904. This set of specifications was endorsed by the American Institute of Architects, the American Railway Engineering and Maintenance of Way Association, the Association of American Portland Cement Manufacturers and the American Society of Civil Engineers and may hence be considered the standard specifications.

The following are noteworthy examples of individual efforts along this line. Porter investigated the lack of uniformity in cement testing. Maclay, Lundteigen, Lewis and Taylor made a study of the accelerated tests for constancy of volume. Lazell showed the lack of uniformity in standard sieves. Meade proved the sieve test to be inadequate for determining fineness in cements ground by different processes. Taylor investigated the influence of aeration on specific gravity. Spaulding, Jamison, Meade and Taylor have published treatises upon the subject of cement testing.

Much improved apparatus for testing cement has also been perfected in this country. Jackson and McKenna have both devised apparatus for determining specific gravity. Gilmore's needles were for a long time used for testing the setting time of cement, and now that the Vicat apparatus has been recommended Bramwell has simplified this. The Fairbanks Co. manufactures an improved form of testing machine which is much used and possesses many points of advantage over its standard German counterpart, the Michaelis machine. Olsen and Riehle have also brought forward excellent testing machines which are much used in this country.

Much has also been done on improving methods of analysis. The New York section of the Society of Chemical Industry appointed a committee to investigate the subject as did also the Lehigh Valley section of the American Chemical Society. Both committees reported and advised methods of analysis. The New York section committee reported a somewhat long but very accurate scheme of analysis, while the Lehigh Valley section committee attempted merely to unify the existing methods and eliminate the seriously objectionable features from these. Both

reports embodied much research work, painstaking investigation and laborious correspondence, and while probably neither method is extensively used just as published, the agitation over the matter accomplished much. Hillebrand's valuable paper upon silica determinations also threw much light upon the subject. The rapid determination of lime in raw materials is now largely made in this country by the method of solution in standard acid and titration of the excess of the latter with standard alkali. It has been found quicker and more reliable than the one of measuring the volume of carbon dioxide liberated, so largely used in Europe.

Newberry's method of determining magnesia by precipitation with a known volume of standard caustic soda is also much used as is Jackson's photometric method for sulphur. In 1901 the writer published his book on the "Chemical and Physical Examination of Portland Cement" which was the first book in any language treating to any extent of the analysis of Portland cement and its raw materials. Frequent papers upon the subject of cement analysis have also been published by W. B. Newberry, Hillebrand, Peckham and the writer.

NAZARETH, PA.

## NOTES ON THE USE OF PEAT.

BY CULLEN W. PARMELEE.

Received July 9, 1906.

THE purpose of this paper is to review certain phases of the peat industry which are of especial interest to the agricultural chemist. As we know, the industry in all its various forms is of great antiquity on the continent of Europe and at the present time peat is being studied systematically at government experiment stations, a considerable periodical literature is devoted to the matter and there are a number of societies interested in developing its uses. In this country the industry has never flourished heretofore, chiefly for economic reasons. Of late, however, interest in the matter has been growing, and it will probably be only a short time before we give peat the same amount of serious study that it is having elsewhere.

The first point to which I would call your attention is the importance of the recovery of swamp land. Parsons, in a recent bulletin published by the New York State Geological Survey, states that "it is estimated that one-twentieth of the area of that state is swamp land" and he points out that unimproved land is assessed at about \$5 per acre and the drained land sells ordinarily at \$200 to \$500. A similar condition undoubtedly exists in all our northern states to a greater or less degree. The practical value of this is twofold; first, the possibility of increasing the taxable wealth; second, recovering the cost of draining by utilizing

the peat removed. Similar work is done in Holland with the result that peat is the common fuel.

With respect to the usefulness of peat for agricultural purposes, the past forty or fifty years has seen a very decided change in views. In 1866, Dr. Samuel Johnson produced his very interesting book on "Peat and Its Uses." It was founded upon his observations and experiments, and his conclusions were based upon the knowledge of agricultural chemistry as understood at that time. During the years which have passed, this branch of chemistry has developed marvelously, and we cannot accept in their entirety the opinions which he gave then. For instance, with the abundance of cheap concentrated fertilizers at hand it would be foolish now to attempt to use peat as a fertilizing material. The labor of digging and spreading material having from 70 per cent. to 80 or 85 per cent. water would be too costly and the time necessary for it to become effective would be too long. In isolated communities under certain favorable circumstances it may be permissible but not otherwise.

The most important use of peat as far as the agriculturist is concerned is undoubtedly its use as litter and subsequent use as compost. Of course, not all varieties of peat are available. Only the soft fibrous material, free from lumps can be used. At present a considerable quantity is used in this country in large stables such as those of breweries, department stores, etc. We import almost all, getting it from Holland. In this country there is only one plant producing peat litter and this is located in Indiana. Not all peat litter has equal absorptive power but a good sample will absorb eight times its own weight of urine while straw absorbs only three times its weight. Moreover, peat has the advantage of preventing decomposition and loss of ammonia. As a compost material, the litter has not only the advantages named but also that of possessing a considerable nitrogen content, which, of course, is increased by that absorbed as a bedding. These matters have, however, been emphasized by other writers who give greater detail than is here necessary. I merely wish to repeat it in order to draw attention to a neglected opportunity.

A method of utilization which is at present finding considerable development is the employment of powdered peat as a filler in fertilizers. For this purpose the earthy varieties of peat are available. Here it serves the purpose of preventing the formation of lumps or crusts of hygroscopic materials. The fertilizer is consequently more easily spread. At present there are three factories operating in New Jersey and one in Illinois and possibly others elsewhere. Besides this use it is said to be used as a diluent for the preparation of low-grade dried blood.

The question naturally arises, what valuation is to be allowed for the nitrogen so introduced? It is quite unlikely that the peat



\* is used primarily for the nitrogen it contains, but it is there and should be differentiated from the other more available forms. Regarding this point there seems to be a wide divergence of opinions among certain authorities. Stutzer ("Die Behandlung und Anwendung des Standdüngers") says that the nitrogen of peat has no value because of the long interval of time required to render it available. Storer, in his book on agriculture, recognizes its comparative inertness but states "that it is a matter of familiar observation and experience that the peat nitrogen may be made to contribute to the support of crops and that it has consequently a considerable money value." He also quotes Nessler as follows: "Although the nitrogenous constituents of peat decompose in the soil more slowly than the altered ossein in meal from steamed bones they do nevertheless in some cases decompose more quickly than the nitrogenous components of wool, or than the ossein in coarse meal from raw bones or than those in leather meal, either that or from torried leather."

As to the quantity of nitrogen to be found in peat, Dr. Johnson reports that he found upon the examination of thirty samples from Connecticut an average of 1.5 per cent. with a maximum of 2.9 per cent. In the course of a study of New Jersey peats, 123 samples have been examined in my laboratory. The nitrogen has ranged from 0.74 per cent. to 2.83 per cent. with an average of 1.75 per cent.

RUTGERS COLLEGE,  
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## NEW BOOKS.

ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By HARRY C. JONES, Professor of Physical Chemistry in Johns Hopkins University. New York: D. Van Nostrand Co. 1906 viii+212 pp. Price, \$2.00.

The author states that the contents of this book had been published previously, as a series of articles, in the *Electrical Review*; the present work is a revised edition of these articles. "The aim of the writer has been to present the more important facts and conclusions in connection with the work on the electrical nature of matter and radioactivity as far as possible in non-mathematical language. \* \* \* While the work is written in semi-popular style, the attempt has been made to treat the subject with scientific accuracy." A perusal of the book shows that Professor Jones has accomplished very satisfactorily the objects announced in the preceding lines quoted from the preface.

The first four chapters deal with the electrical conductivity

of gases, the nature of the electrons constituting the cathode rays, and the evidence of the electrical nature of matter. In the fifth chapter, X-rays and Becquerel or  $\beta$ -rays, and the identity of the latter with cathode rays are discussed. The next six chapters treat of the discovery of radium and of the phenomena of radioactivity. These are followed by three chapters on radioactive emanations and induced radioactivity. The concluding four chapters deal chiefly with the spontaneous transformation of matter and the explanation of the phenomena of radioactivity by means of the disintegration hypothesis and the electron hypothesis regarding the nature of the atom.

There are numerous references to the original literature, but no attempt has been made at completeness in this direction. There is a good index. A few misleading or erroneous statements exist. On p. 141 it is stated that after the separation of UX, the remaining uranium was not appreciably radioactive. This is of course true if the activity is measured photographically, but electrical measurements show that the ionizing power of uranium is but slightly altered by the removal of UX. On p. 147 it is stated that thorium precipitated three times by ammonia is only about one one-hundredth as radioactive as ordinary thorium; the correct statement is found on p. 193. The book is well up-to-date and includes discussions of much of the most important work of the year 1905. It will give the general reader an adequate idea of the nature of the most important achievements in this field of science. It will also serve as a good introduction to the advanced treatises of J. J. Thomson and of Rutherford and to the original literature, for those who wish to study the subject thoroughly.

H. N. McCoy.

LECTURE-NOTES ON CHEMISTRY FOR DENTAL STUDENTS. By H. CARLTON SMITH, PH.G. New York: John Wiley & Sons. 1906. viii+273 pp. Price, \$2.50.

This course in dental chemistry includes the following subjects: Qualitative Analysis, Dental Metallurgy, Volumetric Analysis, Microchemical Analysis, Organic Chemistry, Physiological Chemistry, Digestion, Urine. If the students of the Harvard Dental School, for whom the course was prepared, have found it sufficient for their needs, they must be made of better stuff than ordinary students. For if the latter were reasonably familiar with elementary general chemistry, it seems clear that only the

most intelligent of them could profit by the brief treatment, which some of these topics receive. The sections on organic and physiological chemistry are painfully concise.

It is doubtless convenient to have in concise form "the data that are most likely to be of use in practical work," but students should have more than this. In the chapter on dental metallurgy is found much interesting information regarding alloys, amalgams, cements, solders, etc. In another chapter many local anesthetics are described. Nine half-tone plates with 54 figures of the crystals and the other bodies most likely to be found in micro-chemical study of the saliva, the urine, mouth-washes, and other substances of interest to dentists, should be of value to student and practitioner alike.

L. B. HALL.

CONGRESS OF ARTS AND SCIENCE, UNIVERSAL EXPOSITION, ST. LOUIS, 1904. Edited by HOWARD J. ROGERS, A.M., J.L.D., Director of Congresses. Volume IV: Physics, Chemistry, Astronomy, Sciences of the Earth. Boston and New York: Houghton, Mifflin & Co. 1906 x+766 pp. Price, \$2.50 net.

The addresses presented before the Congress of Arts and Science at St. Louis, are being published in eight volumes, of which Vol. I contains the addresses on the subject of philosophy and mathematics and Vol. IV the addresses of most interest to chemists and physicists. Vol. IV contains the following addresses: The Unity of Physical Science, R. S. Woodward. The Fundamental Concepts of Physical Science, E. L. Nichols. The Progress of Physics in the Nineteenth Century, Carl Barus. The Relations of the Science of Physics of Matter to Other Branches of Learning, A. L. Kimball. Present Problems in the Physics of Matter, F. E. Nipher. The Ether and Moving Matter, D. B. Brace. The Relations of Physics of Electrons to Other Branches of Science, Paul Langevin. Present Problems of Radioactivity, Ernest Rutherford. On the Fundamental Conceptions Underlying the Chemistry of the Element Carbon, J. U. Nef. The Progress and Development of Chemistry during the Nineteenth Century, F. W. Clarke. Inorganic Chemistry—Its Relations with the Other Sciences, Henri Moissan. The Present Problems of Inorganic Chemistry, Sir William Ramsay. The Relations of Organic Chemistry to Other Sciences, Julius Stieglitz. Present Problems of Organic Chemistry, W. A. Noyes. The Relations of Physical Chemistry to Physics and Chemistry, J. H. van't Hoff. The

**Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory**, A. A. Noyes. **Problems in Nutrition**, Otto Cohnheim. **The Present Problems of Physiological Chemistry**, R. H. Chittenden. The last half of the volume contains six papers upon astronomical subjects and sixteen papers upon sciences of the earth. W. A. N.

**FOOD AND NUTRITION. LABORATORY MANUAL.** By MISSES BEVIER AND USHER, Household Science Department, University of Illinois. 1906-1907. 45 pp. Price, \$1.00.

The book is essentially a set of brief laboratory directions dealing with the chemical properties of the "proximate principles" and organic compounds which accompany them in the common foods. It also touches very briefly upon some of the processes of digestion. The successful use of the manual certainly presupposes a fairly comprehensive acquaintance with several of the biological sciences—an experience more extensive than is usually accorded to students of household economics.

The most serious criticism, perhaps, applies to the selection of subject-matter for discussion. Some of the text involves controversial questions (*e. g.*, the adequate classification of proteids) which must at most have a very superficial value. Additional topics (*e. g.*, the chemistry of purins) might advantageously have been included because of their peculiar significance in nutrition. The digestion of fats also deserves mention in a course which presents lecithins and fats in some detail, and considers the other familiar types of enzyme action.

The authors deserve credit, however, for attempting to indicate the broad applications of physiological chemistry to the problems of daily life. LAFAYETTE B. MENDEL.

**LABORATORY MANUAL OF GENERAL CHEMISTRY.** By THOMAS EVANS AND J. F. SNELL. Fourth Edition. University Press, University of Cincinnati, Cincinnati, Ohio. 1905. 8vo. 70 pp. Price, 50 cents.

This laboratory manual contains twenty-nine practice exercises on the non-metallic elements and compounds and eighteen on the metals. The directions for making the experiments are carefully written. A few quantitative experiments are brought in quite early in the course. These are: measurement and reduction of gas volumes, definite and multiple proportions, synthesis of water, weight of a liter of oxygen and the equivalent weight of zinc.

Some of the more salient properties of solutions, such as saturation, supersaturation, ionization and hydrolysis, are illustrated qualitatively. The experiments illustrating mass action are well selected and with accompanying lectures by the instructor can not fail to give the student a good idea of this subject. Additional questions requiring reasoning and study on the part of the student would have been an improvement. Taking it altogether, however, the newer views as well as the older descriptive facts are illustrated and the course as outlined is a very good one for beginners in chemistry.

EDWARD H. KEISER.

LABORATORY EXPERIMENTS TO ACCOMPANY OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH AND CLAUDE FREDERIC WALKER. New York: The Macmillan Co. 1905. 29+104 pp. Price, 50 cents.

The experiments in this laboratory manual are divided as the text-book which it is to accompany into two parts, one inductive and the other descriptive. In the first or inductive part, which consists of 29 pages, there are given experiments to illustrate chemical change, elements and compounds, chemical equivalents (four quantitative experiments), hydrogen, oxygen and oxides, water solution, hydration and hydrolysis, air and nitrogen, electrical equivalents and ions, acids, bases and salts, action and equilibrium.

In the second or descriptive part the elements are taken up in groups according to the periodic system of classification. The chief properties of each element are shown by qualitative experiments. There are constant references to the text-book for equations and explanations.

Taking the book as a whole, it contains a very good course in descriptive chemistry, and the student taking this course will, if he has a good memory, learn many facts concerning the elements and compounds and he will have had good practice in writing reactions. There are, however, very few questions asked him and he can get all his explanations in the text-book. There is nothing to make him think and reason. It would have been an improvement if he had been made to reason out the connection between the facts that he observes in the second part and the laws and principles of the first part.

EDWARD H. KEISER.

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## SOME CONDITIONS INFLUENCING CONSTANCY OF VOLUME IN PORTLAND CEMENTS.

BY EDWARD DEMILLE CAMPBELL AND ALFRED H. WHITE.

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WHATEVER other faults an engineer may forgive in Portland cement, he demands that it shall be reliable and perform its duty for an indefinitely long number of years without deterioration. He dare not use a cement which may change its volume after it forms part of an important structure and thus cause the development of enormous internal strains. Instances of how powerful these strains may be, can be seen by any one thoughtful enough to observe the cement sidewalks over which he passes. The experiments here described form part of a series made with the view of studying the effect of changes in chemical composition upon the properties of finished cement, and especially upon that most important one of constancy of volume. The portion presented in this paper considers a range of composition quite common in American practice where the cement is not very highly limed and the percentages of alumina and iron oxide are together less than half the silica.

These cements have nearly all been under observation for five years, so that we feel warranted in presenting conclusions drawn from a study of their behavior during this period. The chief evidence is supplied by direct micrometric measurements of changes of volume undergone by bars of neat cement either lying in water at room temperature or kept in air at room temperature.



Such measurements were first carried out by Professor Bauschinger, of Munich, many years ago in an apparatus devised by him which bears his name. Measurements have since been made by others and have, in spite of some conflicting evidence, shown quite clearly that good cements expand somewhat in water and contract in air. These measurements have, however, been nearly all made by engineers upon commercial cements concerning which exact knowledge was lacking as to details of method of manufacture, temperature of burning, composition, and age since burning. The present experiments have so far as possible taken account of all these factors and it is believed present a more nearly quantitative estimate of their value than has hitherto been attempted.

Our measurements of change in volume have all been made upon bars of neat cement, and not upon mixtures of cement and sand or crushed stone, such as are used in practice. This added material, so far as constancy of volume is concerned, acts simply as a diluent for the cement. The change of volume due to the cement will vary with the percentage of cement and the relative area of empty spaces, which will depend upon the coarseness of the crushed stone used and the firmness with which the concrete is tamped into place. The use of bars of neat cement eliminates these large variables and allows a close comparison of results between the different kinds of cement. When applying these measurements of change of volume to concrete, it will be necessary to apply an arbitrary factor which will vary with every local condition, and cannot be considered here.

The behavior of Portland cement in concrete kept constantly or usually wet is entirely different from that which is kept dry, and demands separate treatment. The more complicated case of cement bars stored in water is first considered, and afterwards the relatively simple behavior of cement kept in air is treated.

After a brief consideration of the methods and apparatus employed, the paper divides itself into:

- I. The influence of free lime and the effect of aging such cements.
- II. The influence of free magnesia and the effect of aging such cements.
- III. Some considerations determining the form in which lime and magnesia exist in cement including a preliminary study of the

probable equilibrium between free and combined lime, and free and combined magnesia in cements.

#### METHOD OF MANUFACTURING CEMENTS.

Where cements were to be burned in the laboratory each raw material was dried, thoroughly mixed and analyzed. The marls employed were ground to pass a 100-mesh sieve before using. All the cements described in this paper were made from a single clay which was not finely ground, but was disintegrated with water before mixing with the finely ground marl or other source of calcium carbonate. This method of disintegrating the clay left sand in suspension, and in calculating the proportion of basic material to be added, the assumption was made that silica in the form of quartz sand too coarse to pass a 100-mesh sieve was practically inert. The amount of coarse sand in the clay was determined and the necessary allowance made for it. Since one clay is used in all these experiments the results are strictly comparable with one another. The composition of the clinker as reported is calculated exclusive of this sand, which could average about  $2\frac{1}{2}$  per cent. of the weight of the clinker.

TABLE I.—COMPOSITION OF RAW MATERIAL.

	No 5 clay.	L. W. marl	S. L. marl.	M. & W. marl.
SiO <sub>2</sub> .....	46.91	1.21	0.90	1.36
Al <sub>2</sub> O <sub>3</sub> .....	15.89	0.25	0.20	0.55
Fe <sub>2</sub> O <sub>3</sub> .....	5.10	0.25	0.39	0.36
CaO.....	8.25	52.89	51.51	50.03
MgO.....	3.90	0.89	1.68	1.95

The raw materials were mixed with enough water to make a thin slurry, evaporated with frequent stirring to the proper consistency, moulded into cubes and burned in the laboratory rotary kiln as described in preceding papers from this laboratory.<sup>1</sup> Varying percentages of calcium sulphate in the form of plaster of Paris were added to the clinker, and the whole was ground till it practically all passed a 100-mesh sieve.

#### DESCRIPTION OF MICROMETER FOR MEASURING CHANGE OF VOLUME.

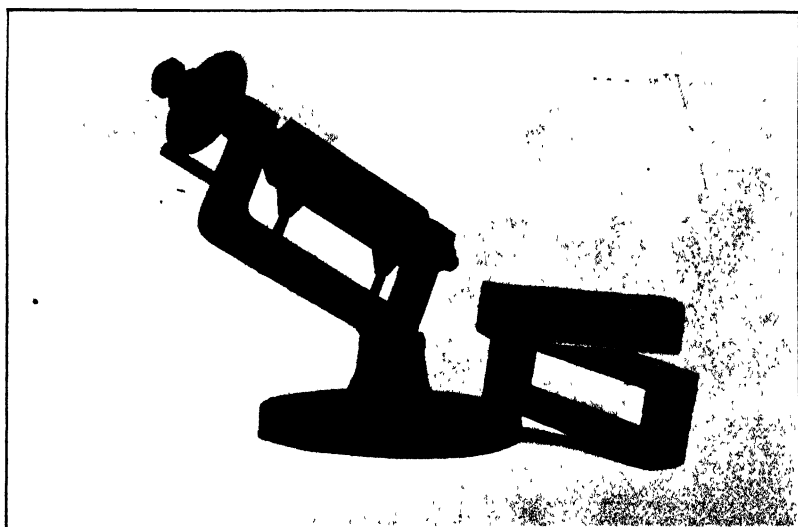
The change in volume was determined by measurement in a micrometer which possesses decided advantages in simplicity over the Bauschinger apparatus. As will be seen from the illustration, the rectangular bar is supported by two forks at an

<sup>1</sup> This Journal, 24, 248, 969; 25, 1103; 26, 1142.

angle of about  $45^{\circ}$ , so that the bar rests by its own weight, with the embedded glass plate against the lower contact piece of the micrometer. The forks compel the bar to always take the same position when being measured, provided the same surface and the same end are placed upward each time. This arrangement always insures the same point of contact for the two ends of the micrometer and eliminates any error due to inequalities in the embedded glass plates. The upper part of the micrometer consists of a screw advancing 1 mm. at each revolution provided with a graduated disc of 50 mm. diameter divided into one hundred parts, each division thus being large enough to enable thousandths to be estimated. The final pressure exerted on the bar is controlled by a friction head turning on the spindle of the micrometer screw.

The expansion bars are made in a split mould 25 mm. square and 102.5 mm. long. Before putting the cement into the mould, a small glass plate is fastened by fine copper wire firmly against each end of the mould so it shall be in the center of the end of the cement bar. These glass plates are cut from microscope slides and are about 12 mm. square. All four edges of each plate are ground to a bevel of about  $45^{\circ}$  and it is placed in the mould with the small surface against the metal. This insures the firm embedding of the glass in the cement. When these glass plates have been carefully cleaned and thus wired to the ends of the mould, the latter is filled with the cement to be tested in the same way as a briquette mould, special care being taken to insure thorough bedding of the glass plates. After striking off smooth, the mould is allowed to stand in moist air, and when firm enough the experiment number is scratched in. After twenty-four hours in moist air in the constant temperature room, the fine wires holding the glass plates are cut close to the bar, and the bar removed and measured. The brass mould was made 102.5 mm. long because the ordinary microscope slides from which the glass plates are cut average 1.25 mm. in thickness so that the length of the prism of cement on which the expansion is measured is 100 mm. This enables millimeters of expansion to be read directly as percentages.

In making measurements care should be taken that the glass plates are carefully cleaned. The bar is then to be placed gently in the supporting forks, right side up, and allowed to slide gently





against the lower contact piece. It is not to be pressed against it by any force except its own weight. It is easy to insure the same position of the bar in all measurements by seeing that the inscription is always up and in position to be read by the observer. When taking observations, the bar is to be pressed very lightly against the forks with one finger of the left hand while with the other hand the micrometer screw is gently turned until the contact point rests against the upper glass plate. In order to insure firm contact at both ends of the bar the fixed head of the micrometer screw is turned after <sup>the</sup> contact with a pressure about equal to that exerted in winding an ordinary watch. The micrometer is then unscrewed about a half-turn until well clear of the bar and is then screwed down again *slowly*, this time by means of the milled friction head. When contact has again been made, the friction head is carefully turned approximately a revolution, so that the pressure on the expansion bar shall be that due to the friction of the movable head only. The reading of the micrometer is then taken, the head unscrewed until free, the bar loosened and the process repeated. Usually four or five such readings are made on each bar. The maximum variation in a series of five such observations will not exceed 0.003 mm. and is usually not over 0.002 mm. Different observers without more than a few minutes' initiatory practice will duplicate each other's readings within these same limits.

It is best to keep the bars, whether in water or air, together with the micrometer in a room of fairly constant temperature. The temperature coefficients of expansion of iron and cement are so close together that provided the bars and micrometer are at the same temperature, variations of a few degrees in the temperature of the room will not appreciably affect the measurements.

#### INFLUENCE OF FREE LIME.

Free lime has always been recognized as injurious in Portland cements, but it has been difficult to study its quantitative influence, because of the impossibility of determining by analysis how much of the lime in a clinker is free and how much is combined. It was decided to make a cement of otherwise normal composition which should contain a known amount of free lime. In order to provide a standard with which to compare such a cement, a normal mixture was prepared and burned as Expt. 77.

To a duplicate raw mixture was added calcite in grains coarse enough to remain as free lime in the cement (Expts. 78 and 81). These cements were made from L. W. marl and No. 5 clay whose composition has been given in Table I. The normal cement, 77, had the following percentage and molecular composition:

## EXPERIMENT 77.

	Percentage.	Molecules.
SiO <sub>2</sub> .....	24.52	100.
Al <sub>2</sub> O <sub>3</sub> .....	8.13	19.6
Fe <sub>2</sub> O <sub>3</sub> .....	2.79	4.3
CaO .....	61.66	270.7
MgO .....	2.89	17.7

This was burned in the rotary kiln at 1522°, which was as high a temperature as could be carried without causing the clinkers to stick together. The clinker was black, hard and brittle. A portion ground when fresh required 2.5 per cent. plaster of Paris to delay the initial set enough to work. With this amount, the initial set was ten minutes and final set twenty minutes. A pat twenty-four hours in air and twenty-four hours in boiling water remained perfect and hard. Bars 77 A and 77 B were made at that time. Another portion of clinker stored in the laboratory for forty days was ground with 1.5 per cent. plaster of Paris and took its initial set in three minutes and final in fifteen minutes. The pat test as before was perfect. The remainder of the cement with 1.5 per cent plaster of Paris was then stored, ground, an additional six months. Its initial set after that period was eight minutes and final two hours. Expansion bars 77 C and 77 D were made at that time. The further discussion of the behavior of this cement is found in connection with the following experiments. It only need be noted that, as was intended, it proved to be in every way a good cement.

The cements to show the influence of free lime (Expts. 78 and 81) were made from a raw mixture, a duplicate of Expt. 77, to which was added a weighed amount of pure calcite crushed and sized to pass a twelve-, but be retained on a twenty-mesh sieve. This relatively coarse calcite was mixed with the normal slurry which was moulded into cubes, dried and burned in the usual manner. It is fairly certain that such coarse calcite would remain almost wholly as free lime in the clinker. The mixture was burned at 1483°, a temperature a little below the average,

but yielding a strong and apparently well-burned clinker. Assuming that all the lime from the crushed calcite remained in the free state, the clinker would contain 2.80 per cent. of free lime, and have the following percentage and molecular composition.

## EXPERIMENTS 78 AND 81.

	Percentage.	Molecules
SiO <sub>2</sub> .....	23.83	100.
Al <sub>2</sub> O <sub>3</sub> .....	7.91	19.6
Fe <sub>2</sub> O <sub>3</sub> .....	2.72	4.3
Combined CaO.....	59.93	270.7
Free CaO.....	2.80	12.6
MgO.....	2.81	17.7

A portion of this clinker ground with 1.5 per cent. plaster of Paris required 23 per cent. of water for normal consistency and took its initial set in two hours and forty-five minutes. The final set was slow, but not exactly noted. A pat after twenty-four hours in air and twenty-four hours in boiling water was warped loose from the glass and very weak. Neat briquettes made at that time, kept in water and broken after seven days, twenty-eight days and six months showed, respectively, tensile strengths of 295, 630 and 862 pounds per square inch. Two expansion bars were made at this same time, 78 A to be kept in water and 78 B in air. The data of measurements are given in Tables II and IV at the close of the paper and the discussion is given below in connection with the following experiment. The other portion of clinker remaining unground was exposed outdoors in an open box during the month of June and after one month's exposure, was ground with 1.5 per cent. plaster of Paris as before. The cement then took 25 per cent. of water for normal consistency and gave an initial set of three minutes and a final set of five. After twenty-four hours in air and twenty-four hours in boiling water the pat was loose from the glass, slightly warped but very strong.

This cement then was manifestly unsound when fresh, as was to have been expected from the free lime, but behaved much better under the boiling test after the clinker had been stored, exposed to the weather for one month. The unexpected fact shown is that this cement containing free lime was slow-setting when fresh, but after one month's storing became so quick-setting as to be useless. It is also to be noted that in spite of its free lime, the tensile tests up to six months were good.



It was deemed best to duplicate this experiment and Expt. 81 was accordingly made as an exact duplicate of Expt. 78, except that the temperature of burning was slightly higher,  $1502^{\circ}$  as compared with  $1483^{\circ}$  of the previous experiment. It being desired to determine the length of time required to completely hydrate free lime existing in clinker if the clinker was exposed freely to the weather, the main body of the clinker was thus exposed during the summer and samples were taken at the end of each month and tested for soundness by the boiling test. The data of the pat tests are on the next page.

This experiment confirms Expt. 78 in showing a relatively slow set on the fresh cement changing to an extremely quick set on exposure of the clinker to the weather for a few weeks. As would be expected, the presence of free lime caused nearly complete disintegration of the pat made from fresh cement. The progressive improvement in the behavior of the pats on boiling, rising to a perfect pat at the end of three months showed that by this time the free lime had probably become completely hydrated. The cement was still very quick-setting (see No. 4). On further exposure of the clinker to weather for a total of ten months, the pat still remained perfect but the cement with the same amount of gypsum added had become slow-setting, requiring nearly four hours for initial set (see No. 8). Storing the ground cement in the laboratory for the same period had a slight effect in the same direction (see No. 7). The conclusion is therefore reached that the bad effects of free lime may be eliminated by aging the clinker exposed to the weather, or the ground cement under cover. The cement may become very quick-setting during this process, but will probably get slower again, if sufficient time is allowed.

#### BENEFICIAL EFFECT OF AGING CEMENTS CONTAINING FREE LIME.

The beneficial effect of aging these cements has been in part brought out by the preceding study of the boiling tests, but it may be best studied quantitatively from the measurements of the expansion bars kept in water whose data are given in Table II, p. 1300, and discussed here, and from the measurements of bars kept in air which will be discussed under a separate heading further on in the paper.

The influence of free lime in cements used fresh and kept under water is best observed by comparing bar 78 A containing free

Treatment of cement.	Plaster of Paris added.	Water. Per cent.	Corresponding expansion bars.	Initial set	Final set.	
1. Fresh.....	1.5	23	Expt. 78, A and B.	45 min. (?)	1 hr.	Result of pat test 24 hrs. in air and 24 hrs. in boiling water. Warped away from glass, badly cracked and easily rubbed to sand.
2. Clinker 1 mo. to weather.....	1.5	23				Less than 15 min. Warped loose from glass and checked.
3. Clinker 2 mos. to weather... ..	1.5	24				Less than 4 min. Loose from glass but very strong.
4. Clinker 3 mos. to weather ...	$\left\{ \begin{array}{l} 1.5 \\ 2.0 \end{array} \right.$	$\left\{ \begin{array}{l} 24 \\ 24 \end{array} \right.$	Expt. 81, A and B.	Within 1 min. ?	?	Pat perfect.
5. Clinker 4 mos. to weather....	2.0	23				Pat perfect.
6. Clinker 4 mos. to weather. } Ground 4 weeks in lab. }	$\left. \begin{array}{l} 2.0 \\ 2.0 \end{array} \right\}$	23	Expt. 81, C and D.	5 min.	15 min.	Pat perfect.
7. Clinker 4 mos. to weather. } Ground 6 mos. in lab. }	$\left. \begin{array}{l} 2.0 \\ 2.0 \end{array} \right\}$	23	Expt. 81, E and F.	7 min.	30 min.	Pat perfect.
8. Clinker 10 mos. to weather...	2.0	22	Expt. 81, G and H.	3 hrs. 45 min.	5 hrs. 30 min.	Pat perfect.

lime with the similar but normal 77 A. Bar 77 A, which has been immersed in water for five years, showed the gradual expansion usual with good cement and the slight drop in the curve at about six months which is also customary. The corresponding bar 78 A showed the effect of its free lime by an abnormal expansion during the first seven days. During this first week it expanded 0.220 per cent. which is more than the corresponding 77 A showed in five years. It continued to expand at a comparatively rapid but diminishing rate until after two months the rate of expansion had settled down to practically a normal rate, showing that the free lime had become completely hydrated by two months' immersion in water. The later history of the bar shows nothing abnormal, although its high expansion in its early history brings its total after five years to 0.451 per cent.

The effect of aging these cements before use is shown by bars 77 D and 81 B, C, E and G. Bar 77 D was made from the normal cement containing no free lime which had been ground with 1.5 per cent. plaster of Paris and then stored in the laboratory six months. The beneficial effect of aging even a normal cement is shown by its much greater constancy of volume as compared with the fresh cement. At the end of two months its expansion was only one-fifth as much as the fresh cement, and its last measurement showed a total expansion, after four years in water, of only 0.052 per cent. This cement also shows the customary slight contraction in volume after three months which in this case brings its volume slightly less than it was initially. This cement, 77, then, behaves throughout as a well-made cement should.

The similar cement, 78, containing 2.8 per cent. free lime showed abnormal expansion when worked up fresh. Expt. 81, which was a duplicate of 78, was purposely not worked up fresh, but was stored as clinker exposed to the weather for four months.

A portion of it was then ground with 2 per cent. plaster of Paris and an expansion bar was made (81 B) which placed in water showed no more expansion than a normal cement which had aged the same length of time. Another bar (81 G), made from a clinker exposed to the weather ten months, showed little difference in its behavior from a normal cement which had been aged. These bars with the corresponding pat tests indicate that the influence of free lime disappears completely if the clinker is stored open to the weather for four months prior to grinding, and that such

cements will be more constant in volume than will most cements of proper composition but worked up fresh.

THE INFLUENCE OF FREE MAGNESIA ON PORTLAND CEMENT.

It was recognized over twenty years ago that magnesia might be a harmful constituent of cement. In 1888 the German Association of Portland Cement Manufacturers appointed a commission with R. Dyckerhoff as chairman to thoroughly investigate the question. This commission after a series of experiments lasting over five years reported in 1895<sup>1</sup> that they could not agree upon a unanimous report. Dyckerhoff maintained as the result of observations upon cements made by him that more than 4 per cent. of magnesia could not safely be allowed in Portland cement. The majority of the committee dissented from this opinion and cited instances of cements with much higher magnesia content which had stood severe tests and had been under observation for years enough to have developed any defects which might have been latent in them. They maintained that magnesia exerted no ill-effect provided the magnesia was calculated as replacing an equivalent amount of lime in the percentage formula

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 1.8-2.2.$$

The conclusions of the majority of the committee were apparently based not on cements which they had themselves manufactured, but on the analysis of commercial cements high in magnesia which had proved themselves safe.

Four years later other experiments were reported by Oskar von Blaese,<sup>2</sup> who manufactured cements containing varying percentages of magnesia. The raw materials were finely ground and burned in a fixed kiln, and the cements showed throughout a very great constancy of volume. The cements with higher percentages of magnesia showed abnormal expansion, but the conclusion of the author is that 5 per cent. of magnesia is entirely allowable in cements. Further evidence of the influence of magnesia was brought forward by Grauer,<sup>3</sup> who presented in 1902 results of five-year observations on the changes in volume of a number of cements containing magnesia up to 4 per cent. He found that

<sup>1</sup> Thonindustrie Ztg. 19, 473.

<sup>2</sup> Ibid. 23, 214.

<sup>3</sup> Ibid. 26, II, 1031.

magnesia up to this amount exerted no marked harmful influence. Unfortunately, he made no experiments with cements containing over 4 per cent. magnesia.

It is curious that none of these investigators seem to have paid any attention to the possibility that the erratic behavior of magnesia was due to the form in which it existed in the cement. Free lime in cement has always been recognized as dangerous, but, when in proper combination with silica and alumina, it forms the principal constituent of cement. It seemed to us there was a possibility that magnesia, like lime, was harmful only in the free state, and that it might sometimes be in entirely harmless combination.

The first step in investigating this question was to determine whether magnesia could be made to combine with silica and alumina as lime does; in other words to make an all-magnesia cement. This successfully accomplished, the next step was to determine quantitatively the effect of magnesia existing undoubtedly in the free state. The problem then was to apply the knowledge thus gained to the solution of the difficult question of determining the equilibrium between free and combined lime, and free and combined magnesia. It is not claimed that anything more than a successful beginning has been made on this problem of equilibrium, but some light has been thrown upon it.

PREPARATION AND PROPERTIES OF AN "ALL-MAGNESIA" CEMENT.

Expt. 80 was made to determine whether magnesia could possibly completely take the place of lime and produce a hydraulic cement which did not show abnormal expansion. The raw materials used were No. 5 clay (for composition see Table I), and chemically pure hydrated magnesium carbonate containing 36 per cent. MgO. These were so proportioned as to give a clinker of the following percentage composition and molecular ratio. The cement necessarily shows a small amount of lime coming from the clay used.

## EXPERIMENTS 80 AND 82.

	Percentage.	Molecules.
SiO <sub>2</sub> .....	28.91	100.
Al <sub>2</sub> O <sub>3</sub> .....	9.79	20.0
Fe <sub>2</sub> O <sub>3</sub> .....	3.14	4.1
CaO .....	5.08	18.9
MgO .....	53.07	274.7
	<hr/> 99.99	

This was burned at  $1496^{\circ}$ . The clinker was apparently well burned, strong and of good appearance. It was ground with 1.5 per cent. of plaster of Paris. A pat required 21 percent. of water for normal consistency, took initial set in fifty-two minutes and final set in nine hours. After twenty-four hours in air and twenty-four hours in boiling water, the pat was perfect in appearance and firmly adherent to the glass, but if broken loose was weak as compared with good Portland cement and could be easily rubbed to sand between the fingers. Neat briquettes made from this cement and kept in water gave a tensile test of 27 pounds per square inch after seven days and 43 after twenty-eight days with a continuous gain to 162 pounds after two years. The difference shown by these tests between this cement and a regular Portland is one of degree only. A bar made from fresh cement and kept in water showed an expansion somewhat *less* than is normal for fresh Portland cement. The measurements extend for five years and are given in Table II.

A duplicate of this experiment was made as Expt. 82, the only difference being that the temperature of burning was somewhat higher— $1538^{\circ}$ . The clinker resembled that from the other experiment. A portion of the clinker was ground fresh with 1.5 per cent. plaster of Paris as in the previous experiment, required 23 per cent. of water instead of 21 for normal consistency, and set somewhat more rapidly, the initial set being twenty minutes and the final five hours. After subjecting to the boiling test the pat was perfect and stronger than in Expt. 80. After the clinker had lain in the laboratory for two weeks, another sample was ground and a pat was made. The initial set had become retarded in that time to one hour and thirty minutes and the final set to seven hours. After the remainder of the clinker had been stored in the laboratory four months, another sample was ground and an expansion bar made. This bar has been kept in water and under observation for four years, the full table of measurements being in Table II. The expansion at the end of four years is only 0.080 per cent., as compared with 0.100 per cent. on the duplicate experiment, 80, which was burned at a somewhat lower temperature and worked up fresh.

These experiments clearly show that it is possible to make a hydraulic cement whose molecular ratio  $RO:RO_2+R_2O_3$  is practically that of many commercial Portland cements but in

which the lime is almost entirely replaced by, magnesia. This cement clinkers at a temperature about that for normal Portland and yields a cement which, except for its inferiority in ultimate strength, meets all the tests demanded of Portland. In fact five-year measurements in water show it to be superior to most cements in constancy of volume.

#### EFFECT OF ADDED FREE MAGNESIA AND COMBINED MAGNESIA.

The next step was to make a series of comparative tests to determine the effect of adding known amounts of free magnesia and combined magnesia to a finished cement. For this purpose fresh cement clinker was procured from one of our older Michigan mills. This clinker had been put through the ball mill so that most of it would pass a twenty-mesh sieve, but no gypsum had been added to it. It had the following composition:

#### EXPERIMENTS 83 AND 85.

	Percentage.	Molecules
SiO <sub>2</sub> .....	24.54	100.
Al <sub>2</sub> O <sub>3</sub> .....	6.80	16.4
Fe <sub>2</sub> O <sub>3</sub> .....	3.17	4.9
CaO ... ..	63.10	276.9
MgO .....	1.87	11.4

Portions of this crushed clinker were ground with the addition of 1.5 per cent. plaster of Paris, and varying proportions of free magnesium oxide and of crushed magnesian cement from Expt. 82 were added to it. The free magnesia was obtained by burning in the rotary cement kiln chemically pure magnesium carbonate at a temperature of not less than 1500°. The entire set of nine bars was worked up within two weeks. 83 A is cement ground without any addition save plaster of Paris. To B, C, D and E were added, besides, 1, 2, 3 and 4 per cent. respectively of hard-burned free magnesia while to F, G, H and I were added 2, 4, 6 and 8 per cent. of the magnesian cement, Expt. 82, approximately equivalent to 1, 2, 3 and 4 per cent. of combined magnesia. Tensile tests made on ten neat briquettes of each series extending over a period of three years did not indicate that the presence of free magnesia lowered the ultimate strength. Pat tests of the cements containing added magnesia after twenty-four hours in boiling water showed no signs of cracking or warping although occasionally and irrespective of the magnesia content, they were loose from the glass. The test of twenty-four hours in boiling

water is therefore not to be relied on to indicate free magnesia even when present to the extent of 4 per cent.

The data of measurements in the nine bars of this series kept in water up to five years are given in Table III. Examination of the figures shows that the original cement (bar 83 A) showed, during the first three months, a relatively rapid expansion which seems to be characteristic of all fresh cements. During the next month it contracted slightly and slowly expanded again until at the end of a year it had reached the same volume as at three months. This drop in the expansion curve seems to be characteristic of all fresh cement and is probably associated with the usual decrease in ultimate strength of neat briquettes in a corresponding period. From one year to five years the expansion proceeded slowly but continuously. This bar, as well as the others described in this paper, will be kept under further observation.

Bars 83 F, G, H and I, containing 1 to 4 per cent. added *combined* magnesia, show the same general expansion as the original cement, but instead of causing a greater expansion this added combined magnesia has *diminished* the expansion slightly, probably because the added magnesian cement itself undergoes such slight changes in volume. After five years these four bars average 0.134 per cent. expansion while the original commercial cement showed 0.144 per cent.

Bars 83 B, C, D and E, on the other hand containing 1 to 4 per cent. of added *free* magnesia, show the same drop in the curve after three months that the others do, and up to this time there is nothing to indicate the presence of free magnesia. After one year, however, free magnesia to the extent of 2 per cent. or more begins to cause evident expansion, and its effect becomes progressively greater as time elapses, until at the end of five years we note that bar 83 E with 4 per cent. of free magnesia has expanded over 1 per cent. The bar at the end of this period is apparently strong and sound and will be observed further. Summarizing the results at the end of five years, we find the following percentages of expansion:

Original cement.....	0.144	
MgO added. Per cent.	A in free state. Per cent.	B combined. Per cent.
1 .....	0.146	0.130
2 .....	0.203	0.130
3 .....	0.382	0.138
4 .....	1.010	0.135



The above figures demonstrate conclusively that magnesia combined in the form of Expt. 82 does not cause expansion and show that the influence of free magnesia up to 1 per cent. is very slight. The dangers attending the presence of this constituent in larger amounts are forcibly shown by the above figures, but the insidious and slow development of the evil effects of free magnesia require further emphasis. Even cement 83 E with its 4 per cent. of free magnesia would have passed perfectly any standard physical tests, and yet after five years in cold water it has expanded over 1 per cent. and there is no indication that the end is reached. Indeed the expansion during the last year is nearly as much as the total of the preceding four years.

#### EFFECT OF AGING CEMENT CONTAINING FREE MAGNESIA.

After the bars for Expt. 83 were made, a certain amount of the ground mixtures was left. In order to confirm the results of Expt. 83 and also to observe the effect of aging the ground cement, a similar set of bars known as Expt. 85 was made from this surplus material. It was worked up after being kept in a basement cupboard for six months in bottles two-thirds of the time stoppered and the last two months with the stoppers removed. Bars 85 C and D form an addition to the series, being made from the crushed clinker stored a similar length of time in a cupboard but freely open to the air all the time. In all, nineteen bars were made in this series, ten being kept in water and nine in air. Four-year measurements of bars kept in water are given in Table III, while those stored in air are in Table IV.

A study of these figures on the bars of Expt. 85 in water shows that the first expansion, after seven days, averages less than two-thirds as much as in the cement not aged. The next point to be noted is that the contraction in volume observed in fresh cements after about three months is almost eliminated in this aged cement. The change in volume except for one or two slight exceptions is steadily an expansion, but after one year the measurements are still notably below the corresponding fresh cements. The last measurements are after four years with the following results as compared with the fresh cement at a corresponding period.

## EXPERIMENTS 83 AND 85.

	Fresh cement. Per cent.	Aged cement. Per cent.
Original cement.....	0.139	0.105
1 Per cent. free MgO added.....	0.144	0.150
2 " " " " " .....	0.190	0.165
3 " " " " " .....	0.253	0.240
4 " " " " " .....	0.562	0.615
1 " " combined MgO added...	0.129	0.115
2 " " " " " ...	0.124	0.107
3 " " " " " ...	0.130	0.099
4 " " " " " ...	0.130	0.084

The original cement aged six months after grinding and before using shows only 75 per cent. of the expansion of the cement worked up while fresh. The bars to which the magnesian cement was added show similar decreased expansion and the difference in favor of the aged cement is greatest in the cases of the bars with largest additions of the non-expansive magnesia cement. The bars with added free magnesia have, on the other hand, expanded practically as much as the fresh cement.

The net result of this experiment is to confirm the harmful and slowly appearing effect of free hard-burned magnesia in cement. Aging the cement before using retards the expansion for a year or two, but the relief is only temporary for after four years the expansion due to free magnesia is about as bad in the aged as in the fresh cement. The conclusion is therefore reached that aging will not prevent the evil effects due to free magnesia, although it may delay their appearance for a year. This is in contrast to the effect of aging cements containing free lime where the harmful effects of free lime may be completely removed by aging. The failure of the aging process to afford relief from magnesia is undoubtedly due to the extremely slow rate of hydration of this substance, which does not seem to hydrate in air at any measurable rate.

## COARSENESS OF RAW MATERIALS AS A FACTOR CAUSING FREE LIME.

Under the heading "Influence of Free Lime," we have already discussed Expts. 78 and 81 to which such coarse particles of calcite were added that most of it was certain to remain as free lime in the finished cement. The effect of smaller differences in fineness, such as exist in marls from different sources, is shown by Expts. 74, 75 and 79. The L. W. marl used in Expt. 79 (and also in Expts. 77 and 78) was exceptionally uniform and

almost impalpably finely precipitated calcium carbonate. The S. L. marl of Expt. 74 consisted largely of shells. It was ground to pass a 100-mesh sieve but the particles then were much coarser than those of L. W. marl. The M. and W. marl (Expt. 75) was intermediate between the two in fineness.

The effect of these differences in the physical properties of the marl is shown in Expts. 74, 75 and 79 where the three marls are combined with the same clay. Expts. 74 and 79 have nearly the same molecular formulas and are burned at practically identical temperatures. Yet 74 with coarser marl clearly shows free lime while 79 is sound. This is shown not only by the boiling tests but by the expansion bars. Bar 79 A from fresh cement showed after seven days in water an expansion of only 0.025 per cent. and cannot have contained a trace of free lime, while bar 74 A made from cement which had the advantage of being stored in the laboratory seven weeks after grinding and before being made up, showed after seven days in water an expansion of 0.190 per cent., nearly eight times as high as 79 A and only to be explained by the presence of free lime. Bar 74 D, made from the same cement stored as ground cement in the laboratory for seven and a half months, showed only normal expansion and confirmed the results previously observed in Expt. 81, that the effect of free lime completely disappears on sufficient aging.

Expt. 75 (medium grade marl) also shows considerable free lime, as is evidenced by the seven-day measurement on bar 75 A in water with its expansion of 0.200 per cent. The effect of aging in eliminating free lime is similarly shown in bar 75 D where the expansion on the seven-day measurement is reduced to 0.020 per cent. by storing the ground cement seven months.

The chemical compositions and molecular ratios of the cements 74, 75, 77 and 79 are given in the subjoined table.

	Percentage composition.				Molecular composition.			
	74	75.	79.	77.	74.	75.	79.	77.
SiO <sub>2</sub> .....	22.90	22.50	23.43	24.52	100.	100.	100.	100.
Al <sub>2</sub> O <sub>3</sub> .....	7.64	7.72	7.77	8.13	19.7	20.3	19.6	19.6
Fe <sub>2</sub> O <sub>3</sub> .....	2.81	2.70	2.67	2.79	4.6	4.5	4.3	4.3
CaO .....	59.59	62.99	58.92	61.66	280.2	301.5	270.7	270.7
MgO .....	7.05	4.06	7.21	2.89	46.7	26.9	46.0	17.7
CaO + MgO...	.....	.....	.....	.....	326.9	328.4	316.7	288.4

It will be noted that the CaO molecular ratio increases in the order 79, 74, 75, but the difference between 79 and 74 is too small

to account for the decided showing of free lime in 74 while it is absent from 79. The difference must be due to the coarser marl of 74. Neither should the free lime in 75 be ascribed to its somewhat higher lime ratio, for Expt. 105 from finely ground material reported in a previous paper gave a perfectly sound cement when burned at 1475° with higher RO ratio of 315.2 molecules of lime and 19.1 magnesia to 100 of silica. This same mixture, No. 105, before its very intimate grinding failed to give a sound cement even when burned at a temperature above 1600°. The details of this experiment showing influence of fineness of grinding on the clinkering process form the subject of a separate paper already published by one of us.<sup>1</sup>

These experiments emphasize the fact, which most mills now realize, that extremely fine grinding of raw materials is necessary to insure the production of cement which shall be sound, even when fresh.

#### FREE MAGNESIA CAUSED BY COARSENESS OF RAW MATERIALS.

There are five cements available for this discussion. The same lot of clay was used for all of them, but the basic constituents were from various sources, as stated below. The details regarding the manufacture of all of these cements have been given in the preceding portions of this paper. The data most important for this discussion are repeated here.

Expt. 80 and 82. "All-magnesia" cements. Very finely divided. Chemically pure magnesium carbonate used.

Expt. 77. Finely divided L. W. marl.

Expt. 79. Finely divided L. W. marl and finely divided magnesium carbonate.

Expt. 74. Coarser S. L. marl and finely divided magnesium carbonate.

Expt. 75. Moderately fine M. and W. marl.

Expt. No.	MgO. Per cent.	Molecules to 100 of SiO <sub>2</sub> .			Temp. of burning.	Estimated free MgO. Per cent.
		MgO.	CaO.	CaO and MgO.		
77.....	2.89	17.7	270.4	288.4	1522°	none
75.....	4.06	26.9	301.5	328.4	1482	2-3
74.....	7.05	46.7	280.2	326.9	1521	3+
79.....	7.21	46.0	270.7	316.7	1474	2-3
80.....	53.07	274.7	18.9	293.6	1496	none

Of these cements only the first in the table, Expt. 77, has a

<sup>1</sup> This Journal, 25, 1103.

low enough percentage of magnesia to pass the most rigid specifications. As has been shown already, the slight expansion of this cement when kept in water for five years assures us that it contains no measurable amount of free magnesia. The next cement in order (Expt. 75 with 4.06 per cent.  $MgO$ ) has low enough magnesia to satisfy many of the specifications. It is, however, made from a coarser marl and is burned at a temperature which is not extraordinarily high, although it should have produced sound cement from an intimately ground raw mixture. The cement contains free lime, as previously noted. A portion of this cement was stored after grinding long enough to destroy the effect of free lime, and then worked up as bar 75 D, which was put in water and has now been under observation for four years. Its low initial expansion shows that the effect of the free lime has disappeared in the aging process, but its expansion at the end of four years reaches the figure of 0.177 per cent., far too high for a sound aged cement. It may fairly be compared with bar 77 D made from sound cement which had been aged about the same time, whose expansion in the same period was only 0.052 per cent., only one-third as much as the cement under consideration.

This tripled expansion of 75 D as compared with 77 D must, so far as we can see, be attributed to the presence of free magnesia. The amount of this free magnesia may be approximately estimated by comparing it with the measurements on Expt. 85 already reported, where varying amounts of free hard-burned magnesia were added to a sound cement which was then aged similarly to Expt. 75. By comparison with the bars of Expt. 85 we estimate that this cement, 75, contains between 2 and 3 per cent. of free magnesia. The reason for this free magnesia is probably to be sought in the relative coarseness of the raw material, which also prevented all the lime from combining. With finely ground raw materials, cement of this composition and burned at this temperature should show much better combination than this one does.

The third cement in the list, Expt. 74, with 7.05 per cent. magnesia, shows an expansion of the bar 74 D of similarly aged cement, amounting to 0.245 per cent. at the end of four years. In comparison again with bar 77 D the increase of 0.193 per cent. over 77 is attributable in the same way to free magnesia. Again estimating by comparison with Expt. 85, the amount of free magnesia required to give an expansion of 0.245 per cent., we

arrive at the probable amount of free magnesia in this cement as a little over 3 per cent. This was burned at as high a temperature as is usual in practice but was made from shell marl as before noted and therefore contained both free lime and free magnesia.

Expt. 79 has very closely the same magnesia and lime ratios as 74 but was made from much more finely divided marl and was burned at a lower temperature. The amount of free magnesia indicated by the total expansion of 0.177 per cent. (bar 79 C) after four years as compared again with the 0.052 per cent. of bar 77 D indicates that the amount of free magnesia is the same as in Expt. 75, between 2 and 3 per cent. The burning temperature was about the same as 75 and the reason that the free magnesia is not higher is to be found in the finer subdivision of the raw material.

In view of the certain evidence of the presence of free magnesia in this cement, Expt. 79, special attention should be drawn to the fact that even the freshly burned cement stood perfectly the test of boiling a pat for twenty-four hours, and that neat briquettes showed a steady gain in strength from 575 pounds after twenty-eight days up to 911 pounds at the end of three years, with no apparent change at the end of the fourth year. This cement would then have passed all the physical tests required in the standard specifications adopted by the American Society for Testing Materials or the Board of Engineers of the United States Army. Yet it is now expanding at a rate which would arouse grave apprehensions had this cement four years ago been put into an important hydraulic undertaking in defiance of its high percentage of magnesia and relying solely on its good physical tests.

In conclusion and to show that much larger amounts of magnesia than those cited may be completely combined, reference may again be made to the all-magnesia cement, Expts. 80 and 82, which, made from finely ground materials and burned at a not unusually high temperature of  $1496^{\circ}$ , show not a sign of free magnesia.

#### EQUILIBRIUM BETWEEN FREE AND COMBINED LIME, AND FREE AND COMBINED MAGNESIA.

The lack of success experienced in making perfect cements with 4 and 7 per cent. magnesia was due in part to coarseness of

the raw materials in Expts. 74 and 75. The only reproach that can be brought against Expt. 79 is that a higher burning temperature might have produced better results. Yet it was burned hot enough to produce good clinker and a perfectly sound cement judged by all usual standards. It seems comparatively easy to get magnesia into combination in the presence of a small amount of lime as shown in Expts. 80 and 82, but when, as is the case in Portland cements, the amount of lime is many times greater than the magnesia it is probable that the more reactive lime enters into combination before the inert magnesia and that to the magnesia falls the task of displacing the lime until equilibrium is reached. When equilibrium is reached, unless both the lime and magnesia are completely combined, there should be *both* free lime and free magnesia present. Expts. 74 and 75 both show this condition, but on account of the coarseness of the raw materials, it is not safe to assume that the free lime is due to the attainment of equilibrium.

The better case of Expt. 79, when the raw materials are finer, shows free magnesia but fails to show free lime. This may be due to lack of delicacy in the test, for we have no means of judging in advance what percentage of free lime would correspond to equilibrium for a given temperature and proportion of magnesia. It seems, however, plausible that the time of passage through the rotary kiln is too short to allow the attainment of equilibrium, and that part of the magnesia remains uncombined on account of its inertness. Cements burned in fixed kilns like those made in Germany by Dyckerhoff would have a better opportunity to attain equilibrium. Yet Dyckerhoff was not able, except in one instance, to obtain perfect cements with over 4 per cent. of magnesia. Von Blaesé was able with a fixed kiln to obtain cements with higher percentages, which showed themselves quite constant in volume. It is to be noted, however, that the clay used by him was lean, containing less than 40 per cent. as much  $R_2O_3$  as  $SiO_2$ . We believe that the relatively large amount of silica and the long duration of burning furnished the best conditions for bringing the magnesia into the combined state.

Our experiments differ in that they were made in a rotary kiln, and although we are not prepared to state that sound cements cannot be manufactured in a rotary kiln when the raw materials contain large amounts of magnesium carbonate, we feel safe in

saying that if such cements can be manufactured, it will only be by paying the closest attention to the grinding of the raw materials and to the manner of burning, and that in the lack of a rapid test to determine the percentage of free magnesia it is far safer to stick to a 3 per cent. magnesia limit when the cement is to be used for important work under water.

The case of the influence of magnesia on cement seems to us to be parallel to the old discussion of the influence of phosphorus on steel. Many instances may be cited of steels high in phosphorus which have stood physical tests apparently satisfactorily. Yet engineers are unwilling to risk high phosphorus and are now insisting on a much lower percentage of that element in structural steel than was required a few years ago. It is now quite generally recognized among metallurgical chemists that the influence of an element such as phosphorus upon the properties of steel depends more upon the form in which that element exists than upon the total amount, and consequently if reliability is to be secured, the only safe course to follow is to require the objectionable element to be so low as to be harmless even if it exist in its most dangerous form.

The situation would be different provided the raw materials used contained magnesia already in combination with silica, as might be the case with some clays. An experiment has been made in this laboratory to determine how far lime would displace this harmless combined magnesia in burning a cement and throw the magnesia into the dangerous free form, but it has not been under observation years enough to enable us to give any judgment.

#### BEHAVIOR OF CEMENT BARS KEPT IN AIR.

In addition to the bars kept in water, duplicate bars of almost all these cements were kept on a shelf in a basement room of fairly constant temperature throughout the year, and measured regularly. The results of these measurements on bars left in air are given complete in Table IV and group the cements into two distinct classes, those that contain free lime, and those that do not contain free lime. The cements which do not contain free lime all contract in volume, and in a remarkably uniform manner, independent of composition. The smallest contraction noted at the end of four years is 0.300 per cent. and the highest 0.392 per cent. The larger figure is for a perfectly fresh cement (77 B)



and the lower is for the same cement aged six months (77 C). In the same way Expt. 81 shows a contraction on the aged cement of 0.300 per cent. (81 F and H) while the fresh cement (81 A) has a contraction of 0.382 per cent. Free magnesia exerts no measurable influence, the bars of Expt. 85 with added free magnesia up to 4 per cent. being indistinguishable from one another.

Almost all these bars show a fairly regular diminution in volume with the exception of a break between the third and sixth month when there is a slight expansion followed nearly always by a decided contraction at the end of one year. This is probably related to the phenomenon previously alluded to in the review of the behavior of bars kept in water. The changes of volume in bars kept in air and water are in general the reverse of each other, and the simultaneous breaks in the curves are probably more than accidental coincidence but we are not prepared at present to offer an explanation of the underlying causes.

The cements containing free lime are exemplified in Expts. 74, 75 and 78. Bar 78 B, containing 2.75 per cent. free lime, is the only instance of a cement known to contain free lime which was worked up fresh. During the first seven days the contraction was practically normal, but expansion due to hydration of the lime commenced to be evident after that date and continued to increase at an accelerated rate until at the end of nine months the bar had expanded 1.17 per cent. and had cracked so badly that observations were discontinued. Of the other cements known to contain free lime, bar 75 B, aged thirty days ground, showed a contraction for fourteen days followed by an expansion, which at the end of five years amounts to 0.800 per cent. The same cement (bar 75 C) stored seven months showed a normal behavior throughout, contracting regularly up to 0.330 per cent. at the end of four years. Bar 74 B, in which the cement was aged seven weeks as ground cement, still showed the influence of some free lime, for although at the end of five years its volume is less than it was initially by 0.059 per cent., yet this contraction is less than it should be for cement containing no free lime. This same cement, bar 74 D, aged seven and one-half months after grinding, shows a contraction almost as large as a normal cement.

The effect of free lime on cement bars kept in air is to cause expansion, not, however, noticeable until after twenty-eight days. The hydration of the hard-burned lime in air is so slow

that there may be continuous expansion up to five years or more. In case the amount of free lime is unusually high as in Expt. 78, the expansion may be great enough to cause disintegration. The normal behavior of cement bars is to contract in air and free magnesia exerts no measurable influence in this respect. Aging cement diminishes the contraction somewhat.

#### BEHAVIOR OF A CEMENT BAR ALTERNATELY IN WATER AND AIR.

It has been shown that cement bars stored in water normally expand and that bars stored in air contract. It is worth noting the effect of alternate exposure to air and water as bearing upon the behavior of cement sidewalks. A sample of clinker obtained from the same mill as Expts. 83 and 85 was stored in the laboratory for eight months and afterwards exposed to the weather for four months. The clinker was then ground with 1.5 per cent. plaster of Paris and the ground cement stored in the laboratory for five weeks. That this long aging had not caused any deterioration in the cement is shown by the fact that neat briquettes made at the time of the expansion bars gave a seven-day test of 420 pounds with increase of strength up to 737 pounds at the end of two years. From this cement two expansion bars were made and placed in water. 72 A kept in water showed very slight expansion as might have been expected from the long aging, the expansion at the end of four years being only 0.022 per cent.

Expansion bar 72 B was kept in water for four months and like 72 A remained almost constant in volume. It was taken out of the water and left in air for twenty-eight days when it contracted from  $-0.005$  per cent. to  $-0.180$  per cent. On being placed again in water, at the end of seven days it had expanded 0.150 to  $-0.030$  per cent. and it remained practically constant for the next three weeks. It was again taken out of the water and placed in air and again contracted until at the end of twenty-eight days it had a contraction to 0.190 per cent., practically the volume which it had formerly assumed in air. It was now placed in boiling water for twenty-four hours and after cooling again showed an expansion to  $-0.030$  per cent. as before after keeping in cold water.

This large alternate expansion and contraction as the result of alternate exposure to air and water gives some indications of the alternate strains to which cement walks are subject and may

easily account for the appearance of hair cracks so common in such structures, especially where a mixture very rich in cement is used as the top coating.

#### SUMMARY.

Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement but will not become completely hydrated even when the cement is immersed in water, until about fourteen days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. Any evil effects due to the presence of free lime in cements kept under water will be manifested within two months. In case free lime is present in cement used in structures above ground or where it is usually dry, the expansion due to hydration of the cement will be more gradual but several times greater in volume than when the material is under water. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration.

The deleterious effects of free lime may be completely removed by aging the ground cement or storing the clinker to weather until the pat will stand a perfect boiling test. Weathering the clinker for three months is usually sufficient. It is difficult to state the length of time necessary to properly age ground cement to eliminate free lime. It will not ordinarily be less than one month and may be much longer according to the conditions under which it is stored.

Cement which passes a perfect boiling test may safely be assumed to contain no free lime. The expansion of a bar of neat cement containing no free lime when kept in cold water for seven days is usually under 0.040 per cent., but occasionally may go as high as 0.060 per cent. A cement with 2.8 per cent. free lime showed an expansion of 0.220 per cent. in the same period.

The effect of magnesia like that of lime depends less upon its total amount than upon the form in which it exists. Combined magnesia like combined lime has no injurious effect in Portland cement. Magnesia combined with silica and alumina forms a hydraulic cement which is safe but as compared with Portland cement is too weak to be of any commercial value. Free magnesia has no appreciable affect in cement used above ground where it is continuously dry. If the cement is wet for a part or a whole of

the time, the free magnesia will very slowly hydrate and cause expansion. Even where the cement is continuously immersed in water the expansion due to free magnesia is not appreciable until after two months and only becomes distinctly evident after a year. The hydration seems to be only well under headway at the end of the first year and expansion continues at an increasingly rapid rate for at least five years, and probably longer. Aging does not seem to diminish the deleterious effect of free magnesia in cement. This is to be expected, since the rate of hydration of hard-burned magnesia in air is almost imperceptibly slow.

The boiling test for twenty-four hours does not detect free magnesia as it does free lime. Cement containing as high as 4 per cent. of free magnesia has passed a perfect boiling test, yet the last measurement of this cement at the end of five years in cold water showed a total expansion of over 1 per cent., nearly half of which occurred during the fifth year after making.

This slow hydration of free magnesia with its accompanying expansion seems to be the probable cause of the expansion, frequently accompanied by more or less complete disintegration, so often noted in sidewalks, occurring several years after the walk has been laid.

One per cent. or less of free magnesia in cements kept under water causes little noticeable expansion even in neat cement; probably simply filling up the voids. Increased percentages of free magnesia cause cumulatively greater expansion until with 3 per cent. of *free* magnesia the expansion is too great to be at all safe.

In the manufacture of cement from raw materials containing magnesium carbonate, some portion of the magnesia will remain in the free state. This amount will increase with coarseness of raw materials, increasing percentage of lime and increasing percentage of magnesia. If the total magnesia does not exceed 3 per cent. it is not likely that well-made cement will carry enough of this magnesia in the free form to cause injurious expansion under any conditions of service. If the percentage of total magnesia rises above 3 per cent. there will be increasing probability of enough magnesia remaining in the free form to cause injurious expansion in large monolithic structures kept continuously or frequently wet. In structures where suitable provision can be made for expansion joints, a higher percentage of total magnesia is permissible than in monolithic structures. Magnesia should

TABLE II.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume.

All measurements indicate expansion unless preceded by a — sign.

Expt. No.	Days.				Months.					Years.					Remarks.		
	7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.		5.	
74 A	0.190	0.226	0.240	0.240	0.240	0.290	0.310	0.330	0.350	0.363	0.370	0.423	0.447	0.499	0.550	0.582	Free CaO and free MgO.
D	—0.005	+0.005	0.004	0.010	0.024	0.024	0.033	0.040	0.050	0.075	0.102	0.121	0.164	.....	0.245	.....	Aged. Free MgO.
75 A	0.200	0.240	0.265	0.270	0.305	0.305	0.315	0.330	0.350	0.355	0.355	0.383	0.390	0.407	0.370	0.432	Free CaO and free MgO.
D	0.020	0.035	0.045	0.055	0.065	0.065	0.072	0.075	0.095	0.115	0.130	0.136	0.152	.....	0.177	.....	Aged. Free MgO.
77 A	0.038	0.055	0.060	0.070	0.098	0.112	0.120	0.120	0.135	0.132	0.130	0.163	0.158	0.170	0.180	0.190	Good cement used fresh.
D	0.008	0.008	0.011	0.018	0.020	—0.005	—0.005	—0.010	—0.005	+0.015	0.028	0.032	0.040	.....	0.052	.....	After aging.
78 A	0.220	0.260	0.280	0.295	0.340	0.355	0.363	0.385	0.390	0.390	0.390	0.414	0.412	0.421	0.441	0.451	Fresh. Free CaO.
79 A	0.025	0.045	0.050	0.070	.....	0.110	0.168	0.150	0.150	0.151	0.160	0.204	0.218	0.250	0.330	0.310	7.2 % MgO. Fresh.
C	0.005	0.015	0.015	0.010	0.020	0.025	0.030	0.035	0.035	0.076	0.089	0.104	0.127	0.145	0.177	.....	7.2 " " Aged.
E	—0.007	—0.001	—0.001	+0.003	.....	0.032	0.036	0.052	.....	0.095	0.117	0.140	0.140	0.180	.....	.....	7.2 " " " "
80 A	0.022	0.030	0.040	0.040	0.040	0.040	0.040	0.040	0.050	0.032	0.032	0.057	0.062	0.082	0.100	0.102	All-magnesia. Fresh.
82 A	0.000	.....	0.005	0.008	0.010	0.025	0.025	0.010	0.025	0.010	0.010	0.029	0.040	0.059	0.080	.....	" " Aged.
81 B	0.030	0.030	0.025	0.026	0.030	0.035	0.035	.....	0.045	0.063	0.077	0.082	0.090	0.099	0.105	.....	Same as 78, but aged.
C	0.005	0.010	0.010	0.010	0.013	0.005	0.005	0.005	0.025	0.044	0.049	0.051	0.059	0.071	0.070	.....	" " 78, " "
E	0.000	0.000	0.000	0.010	0.020	0.035	0.035	0.035	0.043	0.048	0.050	0.068	0.062	0.081	0.092	.....	" " 78, " "
G	0.020	0.025	0.038	0.038	0.053	0.065	0.065	0.073	0.081	0.086	0.089	0.103	0.101	0.115	0.121	...	" " 78, " "

TABLE III.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume.

All measurements indicate expansion unless preceded by — sign

Expt. No.	Days					Months					Years.					Remarks	
	7.	14.	21.	28.		2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	
83	A	0.030	0.038	0.045	0.055	0.080	0.100	0.080	0.090	0.090	0.100	0.112	0.116	0.132	0.139	0.144	Com. cement fresh.
	B	0.025	0.032	0.039	0.045	0.070	.....	0.075	0.082	0.075	0.095	0.106	0.117	0.134	0.144	0.146	"
	C	0.020	0.030	0.040	0.050	0.073	0.094	0.075	0.096	0.078	0.113	0.133	0.150	0.170	0.190	0.203	"
	D	0.027	0.037	0.047	0.057	0.080	0.092	0.087	0.097	0.097	0.127	0.151	0.168	0.197	0.253	0.382	"
	E	0.030	0.040	0.052	0.065	0.090	0.110	0.104	0.120	0.120	0.158	0.172	0.223	0.290	0.562	1.010	"
	F	0.030	0.038	0.046	0.054	0.070	0.075	0.072	0.076	0.080	0.093	0.106	0.110	0.119	0.129	0.130	"
	G	0.026	0.032	0.040	0.049	0.070	0.089	0.080	0.080	0.070	0.088	0.101	0.107	0.119	0.124	0.130	"
	H	0.025	0.036	0.045	0.055	0.060	0.079	0.070	0.070	0.070	0.090	0.101	0.106	0.118	0.130	0.138	"
	I	0.021	0.030	0.040	0.048	0.060	0.072	0.070	0.070	0.070	0.096	0.104	0.110	0.120	0.130	0.135	"
	A	0.020	0.030	0.040	0.040	0.040	0.050	0.050	0.070	0.088	0.085	0.089	0.094	0.108	0.110	.....	Same cement aged.
85	C	0.015	0.025	0.025	0.025	0.030	0.040	0.035	0.055	0.070	0.067	0.074	0.079	0.091	0.100	.....	"
	E	0.020	0.035	0.040	0.040	0.045	0.045	0.055	0.078	0.098	0.098	0.106	0.122	0.127	0.150	.....	"
	G	0.025	0.035	0.035	0.035	0.055	0.048	0.065	0.085	0.106	0.107	0.124	0.135	0.154	0.165	.....	"
	I	0.010	0.030	0.035	0.040	0.035	0.055	0.060	0.085	0.110	0.115	0.136	0.154	0.185	0.240	.....	"
	K	0.020	0.035	0.040	0.040	0.055	0.060	0.080	0.103	0.134	0.141	0.175	0.199	0.282	0.615	.....	"
	M	0.020	0.025	0.030	0.030	0.043	0.045	0.060	0.070	0.084	0.082	0.093	0.096	0.109	0.115	.....	"
	O	0.015	0.018	0.025	0.025	0.038	0.035	0.045	0.060	0.077	0.074	0.084	0.089	0.104	0.107	.....	"
	Q	0.000	0.015	0.015	0.015	0.030	0.030	0.040	0.058	0.072	0.070	0.080	0.087	0.108	0.099	.....	"
	S	0.002	0.002	0.002	0.003	0.005	0.012	0.022	0.032	0.054	0.052	0.062	0.069	0.081	0.084	.....	"
																	"

TABLE IV.—CONTRACTION OF BARS OF NEAT CEMENT IN AIR.

All measurements represent percentage variation from original volume.

All measurements indicate contractions unless preceded by a + sign.

Expt. No.	Days.				Months.							Years.					Remarks.
	7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.		
74	B	0.129	0.137	0.138	0.139	0.107	0.081	0.060	0.046	0.010	0.110	0.048	0.089	0.077	0.032	0.059	Contains free lime.
75	D	0.015	0.055	0.085	0.135	0.178	0.196	0.205	0.205	0.210	0.200	0.259	0.244	.....	0.260	.....	Aged till free lime removed.
	B	0.115	0.120	0.118	0.110	0.050	0.000	+0.095	+0.155	+0.100	+0.090	+0.240	+0.209	+0.342	+0.739	+0.800	Contains free lime.
77	C	0.040	0.075	0.110	0.165	0.230	0.250	0.290	0.285	0.265	0.328	0.308	.....	0.330	.....	.....	Aged till free lime removed.
	B	0.190	0.220	0.227	0.237	0.240	0.237	0.232	0.240	0.318	0.355	0.314	0.355	0.383	0.392	0.393	Good cement used fresh.
78	C	0.025	0.072	0.108	0.139	0.195	0.222	0.260	0.250	0.255	0.247	0.302	0.282	.....	0.300	.....	After aging.
	B	0.120	0.110	0.100	0.085	+0.080	+0.320	+0.775	+1.110	+1.170	Bar badly cracked.						
79	D	0.078	0.115	0.160	0.208	0.260	0.270	0.310	0.300	0.295	0.292	0.367	0.353	0.380	0.388	.....	7.2 % MgO. Aged.
81	A	0.090	0.120	0.195	0.230	0.275	0.295	.....	0.335	0.315	0.306	0.365	0.355	0.380	0.382	.....	Same as 78, but aged.
	D	0.085	0.170	0.180	0.250	0.225	0.285	0.295	0.285	0.285	0.303	0.353	0.354	0.365	0.375	.....	" " 78, " "
85	F	0.125	0.145	0.145	0.155	0.165	0.172	0.170	0.179	0.235	0.246	0.245	0.293	0.284	0.300	.....	" " 78, " "
	H	0.155	0.180	0.165	0.167	0.170	0.180	0.170	0.176	0.225	0.247	0.242	0.292	0.292	0.300	.....	" " 78, " "
85	D	0.107	0.165	0.180	0.210	0.260	0.260	0.270	0.265	0.265	0.316	0.335	0.366	0.378	0.385	.....	Commercial. Aged.
	F	0.100	0.150	0.170	0.180	0.217	0.220	0.217	0.210	0.204	0.249	0.262	0.307	0.322	0.335	.....	Com. Aged + 1 per cent. free MgO.
85	H	0.135	0.185	0.195	0.205	0.235	0.255	0.240	0.240	0.225	0.273	0.286	0.324	0.337	0.355	.....	Com. Aged + 2 per cent. free MgO.
	J	0.105	0.150	0.160	0.190	0.230	0.225	0.220	0.217	0.206	0.253	0.263	0.305	0.319	0.335	.....	Com. Aged + 3 per cent. free MgO.
85	L	0.110	0.170	0.170	0.200	0.240	0.240	0.240	0.235	0.229	0.274	0.290	0.325	0.346	0.360	.....	Com. Aged + 4 per cent. free MgO.
	N	0.110	0.168	0.178	0.203	0.233	0.230	0.223	0.238	0.228	0.272	0.287	0.323	0.334	0.358	.....	Com. Aged + 1 per cent. comb. MgO.
85	P	0.110	0.160	0.175	0.195	0.230	0.220	0.230	0.235	0.225	0.272	0.290	0.325	0.339	0.355	.....	Com. Aged + 2 per cent. comb. MgO.
	R	0.120	0.165	0.180	0.200	0.225	0.220	0.210	0.225	0.218	0.257	0.277	0.313	0.325	0.350	.....	Com. Aged + 3 per cent. comb. MgO.
85	T	0.110	0.160	0.180	0.190	0.210	0.200	0.200	0.220	0.217	0.264	0.278	0.313	0.311	0.330	.....	Com. Aged + 4 per cent. comb. MgO.

not exceed 5 per cent. total when used even under these circumstances.

An increasingly large amount of cement is being used in the structure of buildings where it will never be exposed to the action of water. There is no ground for believing that magnesia even in the free form would cause trouble under such circumstances. Free lime, however, is more dangerous in these structures than where the concrete is to be kept damp, because the expanding lime increases its volume much more in air than in water. Concrete made from sound cement will normally contract in the air, and this contraction continues according to our measurements for at least five years and amounts with neat cement to about four-tenths per cent. Whether this contraction will be sufficient to seriously weaken structures such as floors deserves investigation.

Any cement worked up fresh will change its volume more than if properly aged. It will show a noticeable drop in the curve representing change of volume after about three months, a period which corresponds to that in which briquettes show a falling off in tensile strength. Cement should always be aged for work where constancy of volume is of the highest importance. The only disadvantage of aging lies in the tendency for a cement to become very quick-setting. If it is aged long enough, it reverts again to a slow-setting cement.

Leaving out of account free lime and magnesia the amount of expansion of a cement is apparently dependent upon the proportion and arrangement of the other constituents. The experiments here reported deal with cements with fairly low lime, and with alumina and oxide of iron also below rather than above the average. We have made cements richer in alumina and oxide of iron and also in lime, but observations have not as yet been carried out for a long enough period of years to warrant generalization. The data so far gathered confirm the general results given above but indicate that these cements higher in lime and alumina will be less constant in volume than those described here.



# ON THE HEAT-TREATMENT OF SOME HIGH CARBON STEELS.<sup>1</sup>

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*Introduction.*—The study of steel and the changes which it undergoes forms one of our most important lines of research at the present day. Our knowledge of the subject has made great advances during recent times and we now know the reason for many of the profound changes of structure and of constitution which take place with changes of temperature. This advance is due in a great measure to the great improvements in pyrometry, to the wide application of metallography and to the use of certain principles of physical chemistry in explaining our results.

From a constitutional point of view steel naturally falls into three groups:

(1) Unsaturated (Arnold): Hypo-eutectoid (Howe), consisting of ferrite and pearlite in the slowly cooled condition. Carbon content less than 0.9 per cent.

(2) Saturated: eutectoid, consisting of pearlite alone. Carbon about 0.9 per cent.

<sup>1</sup> Work carried out in conjunction with Committee F on the "Heat-Treatment of Steel," American Society for Testing Materials.

(3) Supersaturated: hyper-eutectoid, consisting of cementite and pearlite in the normal condition. Carbon content greater than 0.9 per cent.

*Previous Work on the Subject.*—Since Osmond's classic paper<sup>1</sup> on the transformations of structure which take place within the range of the critical points of steel, a vast amount of research has been done. In many cases both high, medium and low carbon steels have been studied and the work of Arnold,<sup>2</sup> Sauveur<sup>3</sup> and Stead<sup>4</sup> has thrown much light on the subject. In other cases, the effect of varied heat treatment on the physical properties and microstructure of some particular steel has been worked out. Fay and Badlam<sup>5</sup> worked with a low carbon steel of 0.07 per cent. carbon and 0.32 per cent. manganese. Morse<sup>6</sup> used a medium carbon, 0.34 per cent. with 0.22 per cent. manganese. Campbell<sup>7</sup> studied a rail steel with 0.5 per cent. carbon and 0.98 per cent. manganese, while Sargent<sup>8</sup> took up the subject with a high carbon steel (1 per cent. carbon).

The Sixth Report of the Alloys Research Committee<sup>9</sup> deals with the heat treatment of a series of eight steels (0.13 to 1.3 per cent. carbon) at temperatures from 620° to 1100°, and works out their mechanical properties and microstructure.

The present work was undertaken along similar lines because there seemed an opening for research work on steels high in carbon.

*Outline of Present Work. Crucible Steel.*—A series of six steels,<sup>10</sup>  $\frac{5}{16}$  inch square, whose analyses are given in Table A were used in the form of 12-inch test pieces. Heats were made in a horizontal cylindrical gas forge. The bars were packed in an inner iron tube 2 inches in diameter which was then placed in the axis of a larger tube  $3\frac{1}{2}$  inches in diameter by means of which heating was done by radiation and was very uniform.

<sup>1</sup> Bull. Soc. d' Euc. 1895, 10, 476 (Osmond and Stead: "Microscopic Analysis of Metals," Lippincott).

<sup>2</sup> J. Iron and Steel Inst. 1901, 1, 175, 1905 2, 27.

<sup>3</sup> Trans. A. I. M. E. 1896, p. 863, etc.

<sup>4</sup> J. Iron and Steel Inst. 1898 1, 145, etc.

<sup>5</sup> Tech. Quart. 1900.

<sup>6</sup> Trans. A. I. M. E. 1899, 729.

<sup>7</sup> J. Iron and Steel Inst. 2, 359 (1903).

<sup>8</sup> Trans. A. I. M. E. 1901, 303.

<sup>9</sup> Inst. Mech. Eng. London, 1904.

<sup>10</sup> The gift of the Carpenter Steel Co., to whom our thanks are due.

The furnace was charged cold and the heating was so regulated that the maximum temperature was reached in about one to one and a half hours. As soon as the temperature was steady, say five minutes, the gas and blast were turned off and the furnace allowed to cool slowly. This took three and a half or more hours.

An exact record of heating and cooling was kept by means of a LeChatelier pyrometer, the hot junction being in the center of the bundle of steels.

Nine heats were made between 650° and 1200°. The temperatures and heat numbers are given in Table B. These temperatures are very close to those aimed at, *viz.*, 650°, 710°, 750°, 800°, 850°, 900°, 1050° and 1200°.

The critical points of each steel had been previously taken and on heating  $Ac_1$  lay between 730° and 740° while on cooling  $Ar_1$  was found to be 710° to 700°.  $Ac_{2-3}$  and  $Ar_{2-3}$  were not detected, however. The above temperatures were therefore chosen so that one heat was below the critical points, one was at  $Ar_1$ , a third just above  $Ac_1$  *i. e.*, to the region where the change from pearlite into the solid solution is complete. The heats to temperatures above this pass through the region of the change  $Ac_{2-3}$  or the solution of cementite (iron carbide) in the solid solution, 1200° producing great overheating.

TABLE A.—ANALYSIS OF STEELS.

No.	C.	Mn.	P.	Si	S
1.....	2.04	0.28	0.014	.....	0.014
2.....	1.94	0.20	0.009	0.17	0.013
3.....	1.72	0.075	0.013	0.20	0.018
4.....	1.61	0.19	0.013	0.19	0.013
5.....	1.04	0.12	0.012	.....	0.017
6.....	0.70	0.068	0.012	0.141	0.019

TABLE B.—HEAT TREATMENT.

Heat No.	Heated to °C.
3.....	650
1.....	715
6.....	760
2.....	800
4.....	855
0.....	905
5.....	950
2.....	1070
8.....	1200
A	As rolled.
X	

All of the heats reached their maximum in one to one and one-half hours with the exception of Z to 1070° which took two hours and twenty minutes to heat up. This was due to trouble with the blast.

The mechanical tests were made on a Riehle testing machine,<sup>1</sup> the elastic limit being determined by drop of the beam and elongation measured in 2 inches.

The figures thus obtained have been tabulated in Tables I to IV and from these tables have been plotted curves I to IV. Instead of following the usual custom and plotting the figures for each steel on a separate sheet, it was found that by making four tables and four curves to correspond, for (1) maximum loads, (2) elastic limits, (3) reductions of area, (4) elongations, a great deal more could be learned of the changes as a whole.

*Summary of Results of Mechanical Tests.*—From an examination of the mechanical properties, microstructure and fractures, it was immediately seen that the steels fell naturally into two groups, *i. e.*, those consisting of pearlite with an excess of cementite or Nos. 1 to 4 and those consisting of pearlite alone (or nearly so), Nos. 5 and 6. It will be noticed how markedly the curves follow the same general directions and tend to coincide with each other.

*Maximum Load.* Table I, Curve I.—Of the first four steels, No. 4 with 1.61 per cent. carbon is the strongest with 160,000 pounds per sq. in. The weakest is No. 1 with 144,000 pounds per sq. in. Heating to 650°, which is far below the critical point, causes a reduction of some 30,000 pounds, while heating to a temperature just above the critical point  $Ac_1$  (760°) brings down the maximum load to approximately the same point for each steel, *viz.*, between 95,000 and 100,000 pounds per sq. in. Heating to higher temperatures has but little further effect until we reach heat 8, 1200°, where the maximum load has dropped sharply some 25,000 to 40,000 pounds and now lies between 70,000 and 58,000 pounds per sq. in. In this heat, as in the case of the bars as rolled, No. 1 is the weakest and No. 4 strongest.

Of the last two steels as rolled, No. 5 with 1.04 per cent. carbon has maximum load of 140,000 pounds and No. 6 with 0.70 per cent. carbon has maximum load of 117,000 pounds per sq. in.

<sup>1</sup> Thanks are due to Professor Woolson, Columbia University, for use of this machine.

TABLE I.—MAXIMUM LOADS IN THOUSAND POUNDS PER SQUARE INCH.

Steel. No.	Carbon. Per cent.	As rolled.		Heat number and maximum temperature in °C.										1070°. Z.	1200°. 8.
		A.	X.	650° 3	715° 1.	760° 6.	800° 2.	855° 4.	905° 0.	950° 5.	990° 0.	1070° Z.	1200° 8.		
1.....	2.04	144.6	144.0	115.4	114.5	98.8	95.6	93.8	95.2	95.2	99.0	99.0	57.4		
2.....	1.94	146.5	146.3	115.2	104.1	95.0	92.0	89.2	95.3	91.8	97.0	97.0	61.3		
3.....	1.72	152.8	154.0	126.0	114.1	100.3	98.0	94.0	94.3	95.0	92.3	92.3	65.3		
4.....	1.61	162.2	153.2	128.1	117.0	98.6	97.7	95.0	97.3	96.3	94.4	94.4	69.8		
5.....	1.04	140.6	141.6	105.4	97.8	86.8	96.6	111.8	115.9	111.5	106.1	106.1	112.6		
6.....	0.70	117.4	116.6	95.2	88.7	85.6	94.3	91.3	90.3	90.5	89.5	89.5	90.0		

TABLE II.—ELASTIC LIMIT IN THOUSAND POUNDS PER SQUARE INCH.

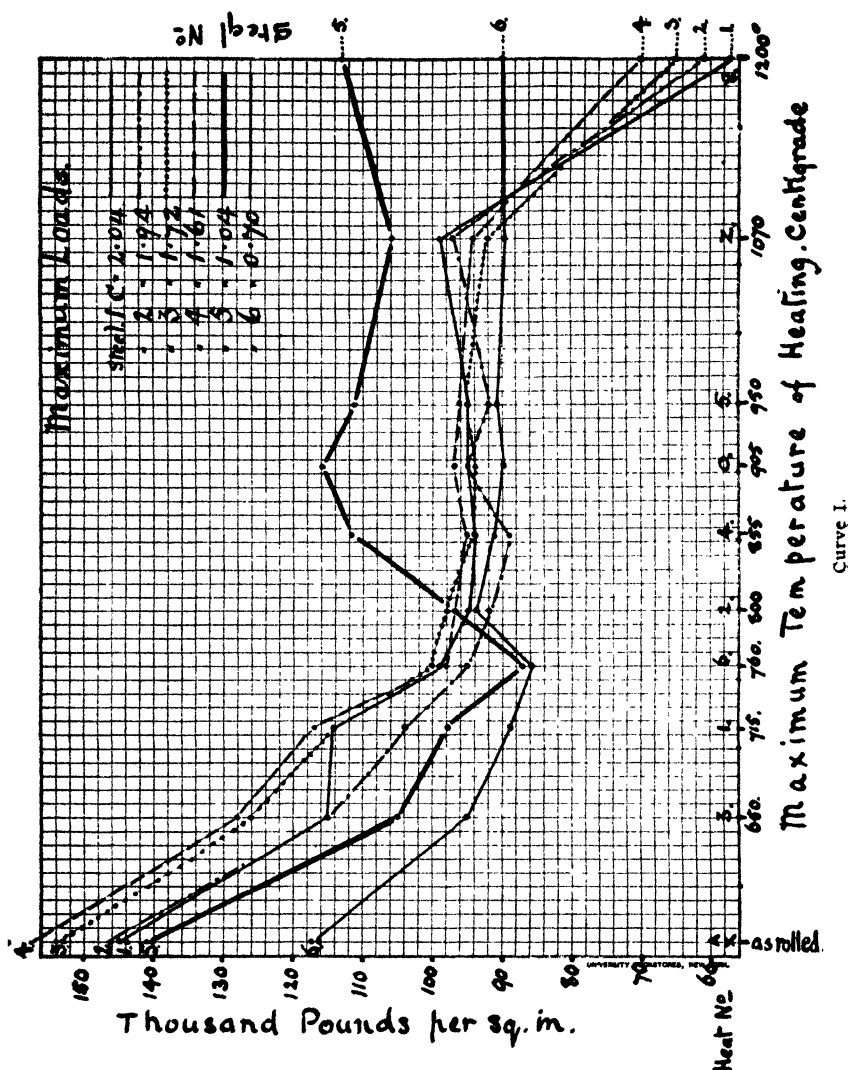
Steel. No.	Carbon. Per cent.	As rolled.		Heat number and maximum temperature in °C.										1070°. Z.	1200°. 8.
		A	X	650° 3.	715° 1	760° 6	800° 2	855° 4	905° 0.	950° 5.	990° 0.	1070° Z.	1200° 8.		
1.....	2.04	101.8	104.2	84.6	83.9	57.7	57.8	55.5	55.3	49.3	49.6	49.6	56.0		
2.....	1.94	91.0	91.5	72.6	68.6	50.5	51.0	49.4	49.8	41.7	47.0	47.0	....		
3.....	1.72	98.7	97.5	78.3	75.7	50.5	48.7	47.9	48.6	45.2	43.1	43.1	50.6		
4.....	1.61	105.2	105.2	85.3	81.3	52.3	53.3	51.3	51.3	48.5	51.4	51.4	....		
5.....	1.04	75.8	75.8	57.7	55.2	44.8	46.6	47.2	50.6	46.8	56.5	56.5	89.6		
6....	0.70	65.3	64.2	53.2	49.7	40.2	42.1	42.1	41.4	39.7	57.3	57.3	58.5		

TABLE III.—REDUCTION OF AREA PER CENT.

Steel. No.	Carbon. Per cent.	As rolled.		Heat number and maximum temperature in °C.									
		A.	X	650°. 3	715°. 1	760°. 6	800°. 2	855°. 4	905°. 0	950°. 5	1070°. Z.	1200°. 8	
1.....	2.04	3.5	3.0	6.5	6.6	16.2	19.6	13.2	12.6	5.8	2.7	0.4	
2.....	1.94	6.5	6.0	8.9	12.0	18.8	15.0	12.1	9.5	12.0	7.6	1.4	
3.....	1.72	5.2	8.7	7.3	18.8	20.5	10.3	12.0	9.6	6.3	4.3	1.0	
4.....	1.61	8.2	9.1	8.3	21.5	34.0	19.1	14.2	9.4	6.8	2.6	1.9	
5.....	1.04	22.7	21.8	36.2	41.5	36.6	21.0	11.3	8.8	10.9	10.6	10.7	
6.....	0.70	27.3	27.0	33.9	45.2	38.7	20.9	20.7	21.8	20.5	17.9	16.8	

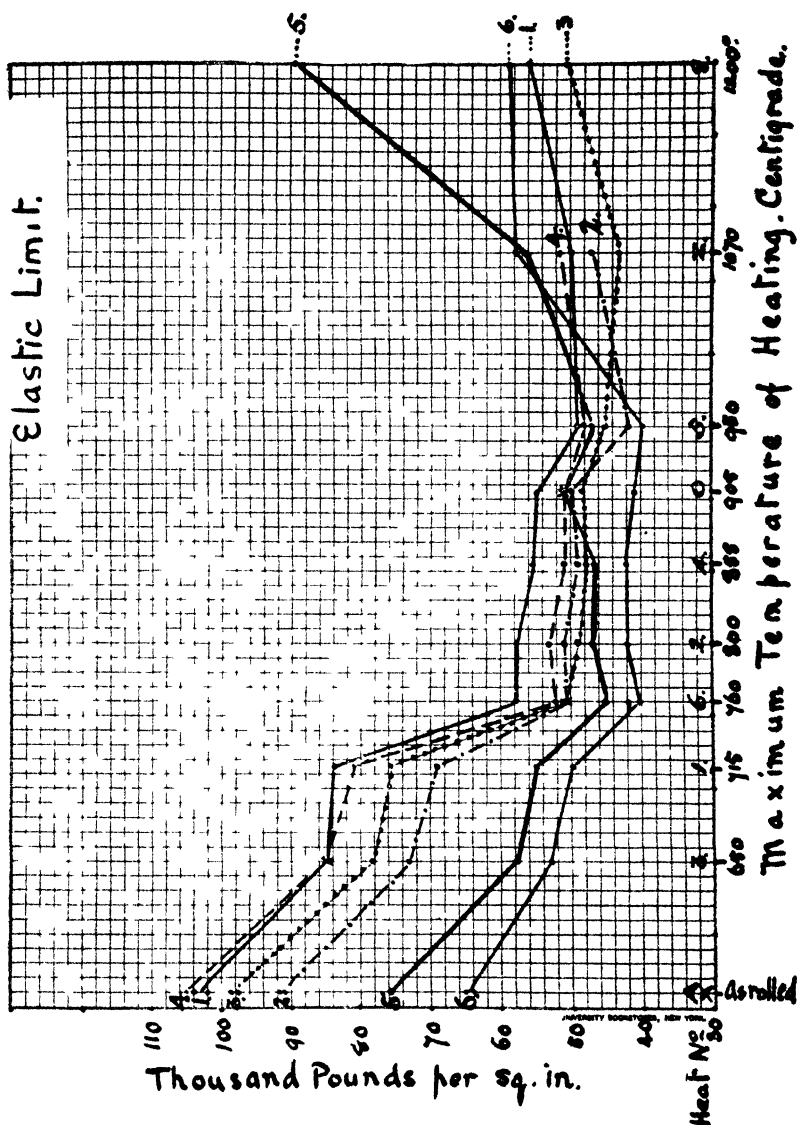
TABLE IV.—ELONGATION IN TWO INCHES.

Steel. No.	Carbon. Per cent.	As rolled.		Heat number and maximum temperature in °C.										1070°. Z.	1200°. S.
		A.	X.	650° 3	715° 1.	760° 6	800° 2.	855° 4.	905° 0	950° 5					
1.....	2.04	4.5	4.0	6.0	7.0	11.5	12.5	12.0	11.5	6.0	4.5	1.0			
2.....	1.94	6.0	6.5	8.0	9.5	15.0	17.0	12.5	7.0	9.5	8.5	2.0			
3.....	1.72	6.5	8.0	8.0	11.5	16.5	10.0	13.5	11.0	7.5	6.0	2.0			
4.....	1.61	7.0	6.0	..	14.5	20.0	18.5	15.0	11.5	7.5	3.5	3.0			
5.....	1.04	13.5	12.0	18.0	22.0	26.5	19.0	13.0	13.0	10.5	11.0	11.5			
6.....	0.70	17.0	17.0	23.0	27.5	27.0	19.0	18.5	18.0	16.5	18.0	16.0			



Heating to 650° and 715° brings down the strength regularly as before, while the 760° heat (just above  $A_c_1$ ) gives the same maximum load of 86,000 pounds per sq. in. for both. In the case of steel No. 5, heating to higher temperatures causes a great rise in strength with a maximum of 116,000 pounds for heat No. 0 (905°). For steel No. 6 the improvement is slight but permanent.

**Elastic Limit.** Table II, Curve II.—For the first four steels the curves have the same general form as for the maximum loads.



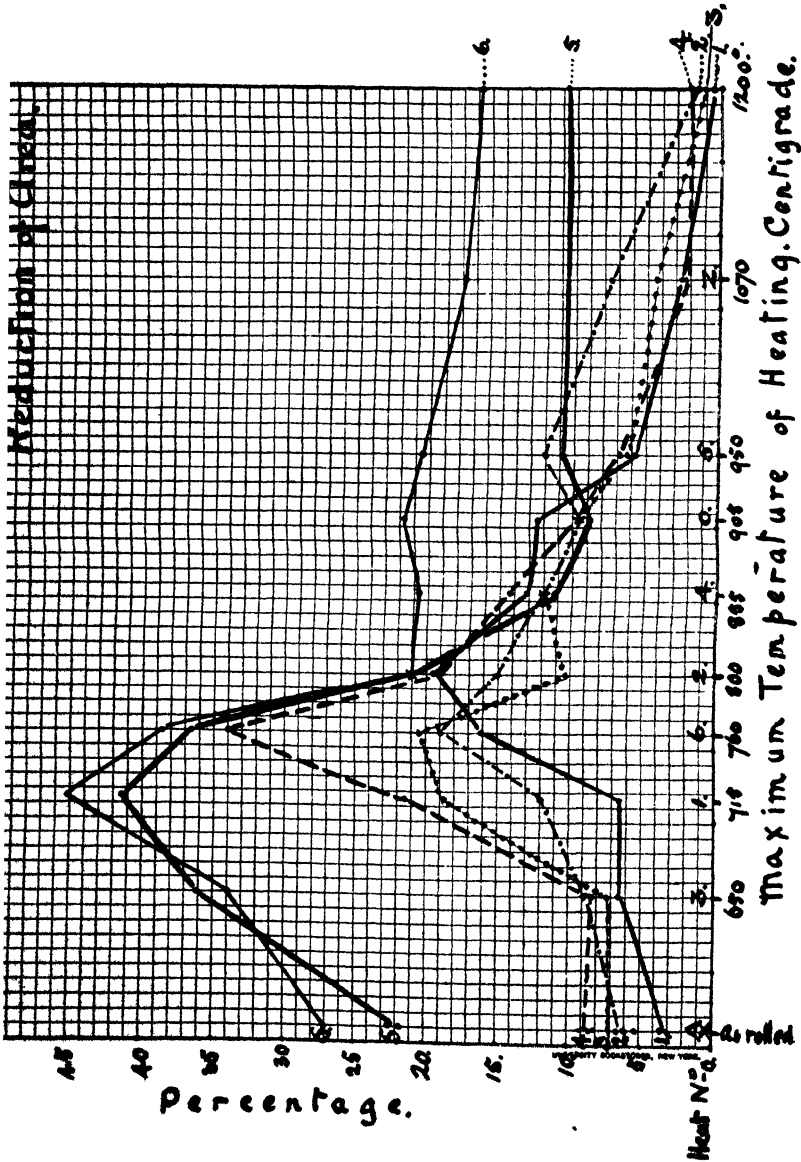
Curve II.

In all, heating to 650° brings about a fall of some 20,000 pounds; heating to 715° gives a slight but regular decrease, while the bars heated to just above the critical point (heat 760°) had an elastic limit down to 50,000–58,000 pounds per sq. in. for steels 1 to 4. For steels 5 and 6 this occurs at 44,800 and 40,200 pounds



per sq. in. In the  $950^{\circ}$  heat, the elastic limit for all of the steels occurs between 40,000 and 50,000 pounds per sq. in.

As in the maximum loads so here heating to higher temperatures ( $1070^{\circ}$  and  $1200^{\circ}$ ) causes an improvement both for steel 5 and steel 6.



Curve III.

*Reduction of Area.* Table III, Curve III.—In general we find that the ductility increases as the strength falls off. For steels 1 to 4 the reduction of area increases till a maximum is reached for the heat just above the critical point,  $760^{\circ}$  (in case of steel 1  $800^{\circ}$ ). In the case of steel 4,  $C=1.61$  per cent., the rise is from 8.2 to 34 per cent., showing some marked change in the structure of the steel.

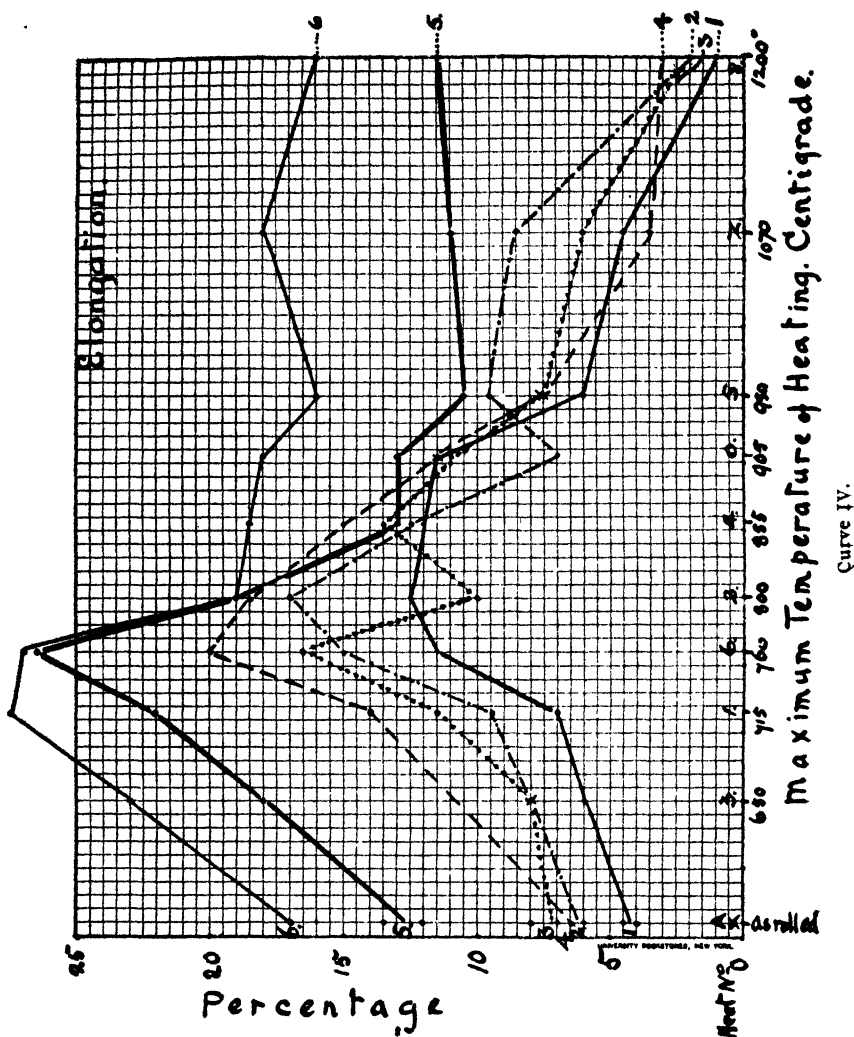
For steels 5 and 6 the maximum occurs in heat 1 to  $715^{\circ}$ , being almost double that of the bars as rolled. The  $760^{\circ}$  heat shows a slight fall, but the next heat ( $800^{\circ}$ ) shows a fall to 21 per cent., or less than half the maximum. Beyond this point No. 6 shows but little further change, being overheated. No. 5 falls away to about 11 per cent. with the next heat ( $855^{\circ}$ ) and then remains constant. It is likewise overheated.

For steels 1 to 4 the  $855^{\circ}$  heat has produced a fall to between 12 and 14 per cent., while further heating produces a uniform decline to less than 2 per cent. for the  $1200^{\circ}$  heat. At this point as in the bars as rolled the figures, with one exception, run in the order of carbon content. The irregularity of steel 3 heat 2 to  $800^{\circ}$  in this and the elongation is due to fracture occurring in the grips.

*Elongation in 2 Inches.* Table IV, Curve IV.—Heating up to a certain point increases the elongation as well as the reduction of area. The maximum for steels 1 and 2 is found in the  $800^{\circ}$  heat, for steels 3, 4 and 5 in the  $760^{\circ}$  heat, while for steel 6, the  $715^{\circ}$  heat gave a slightly higher figure. As in the case of the reduction of area so here we find that heating to higher temperatures causes a falling off. Steel 6 at  $800^{\circ}$  and steel 5 at  $855^{\circ}$  are badly damaged, and further heating has but little further effect. Steels 1 to 4 show a regular falling off until with the  $1200^{\circ}$  heat the elongation lies between 1 and 3 per cent. (steel 2, heat 0 to  $905^{\circ}$  is irregular, due to breaking in the grips). As we should expect, there is a very close resemblance between the curves for elongation and those for reduction of area.

Before attempting to explain the above changes which occur in the physical properties around the critical point  $Ac_1$  and elsewhere, it seems best to examine both the fractures and micro-structure, when it will be seen that here again we have profound changes taking place at the same points.

*Fractures of Test-pieces.*—In Fig. 1 we have the whole of the fractures assembled in pairs in such a way that each horizontal



Curve IV.

row (of pairs) corresponds to one steel varying in heat treatment from right to left; each vertical row on the other hand represents one heat and contains 6 different steels. In Figs. 2 to 13 typical fractures are shown, magnified 6 diameters.

*Steel 1,  $C=2.04$  per cent.*—In Fig. 1 there are two changes noted in steel No. 1. The finest fracture is from heat 2 at  $800^{\circ}$ . Up to this point there is but little change and Fig. 6 may be taken as the type. From heat 2 onwards to heat 5 at  $950^{\circ}$  there is a progressive coarsening of the grain and the appearance of a thin

crystalline border (Fig. 2). Heat Z shows a great change, for the fracture is very coarse and shows up black, with a strong columnar border. This is even more marked in heat 8, 1200°, where the border is one-third of the radius. Figs. 5 and 9 serve as types.

*Steel 2, C = 1.94 per cent.*—The finest fracture occurs in heat 6, 760°, beyond which the grain gets coarser. At heat 5, 950°, in addition to the bright crystalline border there is a marked zone just beneath the surface which is black from graphite. The change can be seen by comparing Figs. 2 and 3. Heating to 1070°, heat Z, completes this precipitation of graphite and the fracture is coarse throughout as in Fig. 4. Fig. 5 shows the fracture of the 1200° heat which is still more coarse, with the strong columnar border as before.

*Steel 3, C = 1.72 per cent.*—Fractures of heats 1 and 6 are very fine. Fig. 6 shows the fracture as rolled and may be taken as the type of these first three steels. Fig. 7 shows that of the 715° heat and is also a type. With increase in temperature above the critical point the fractures grow coarser and the crystalline border shows more and more. Heat Z again shows the marked change to a very coarse fracture throughout, with a strong columnar border, as is shown in Fig. 8. Fig. 9 shows the fracture for the 1200° heat, just as coarse but of lighter color; no graphite.

*Steel 4, C = 1.61 per cent.*—The smallest fracture is that of heat 6, 760°, which is also the finest. Above this point we get a gradual coarsening of the grain with the great change at 1070°, due to marked overheating, as in steel No. 3. There is but little graphite in Z however. The 1200° heat shows the change in color, no graphite present.

Viewed as a whole steels 1 to 4 show the finest fracture just above the critical point. From this point onwards the grain grows coarser and a thin crystalline border shows, which as we shall see later is most probably due to decarburization. At heat Z, 1070°, all the fractures become coarse throughout, with a strong columnar border and black color due to graphite. Heat 8, 1200°, gives an even coarser fracture and the border is at least one-third radius deep. Steels Nos. 3 and 4 also show a change in color at this heat, due to the absence of graphite.

*Steel 5, C = 1.04 per cent.*—The assembled fractures for this steel (Fig. 1) show a marked change. As rolled the fracture shows

a dark core as seen in Fig. 10. Heating to  $650^{\circ}$  yields a smaller fracture shown in Fig. 11. Heat 1 to  $715^{\circ}$  gives the finest fracture, and this is shown in Fig. 5. The  $760^{\circ}$  heat also yields a fine fracture but in heat 2,  $800^{\circ}$ , there is considerable coarsening. Heating to  $855^{\circ}$  causes a marked change and produces a coarse fracture throughout, showing that overheating occurs here. From this point on the fractures are all coarse and Fig. 13, heat Z to  $1070^{\circ}$ , may be taken as a type.

*Steel 6, C = 0.70 per cent.*—The assembled fractures are very similar to those of the last steel, the  $715^{\circ}$  heat yielding the finest fracture. Overheating, however, is seen to occur at  $800^{\circ}$ . The dark center of the bar as rolled (as in Fig. 10) continues to heat 6 at  $760^{\circ}$ . This is apparently due to the outer part of the bar rupturing across the grain while the core breaks like fibre. Thus in steels 5 and 6 overheating occurs at such low temperatures as  $855^{\circ}$  and  $800^{\circ}$ . The finest fracture is given by the  $715^{\circ}$  heat. However, it may be remarked that the finest fracture does not necessarily mean the finest grain in the steel. Reduction of area has taken place and so in steels having grains of equal size, the one with the greater reduction of area would apparently have the finer grain as judged by fracture. When the microstructure is taken into account it is seen that the grain from the  $760^{\circ}$  heat is as fine as, if not finer than, any other.

*Examination of Microstructure.*—Sections were cut from each bar, ground down on an emery wheel, rubbed on emery papers and finally polished with broadcloth and rouge, as has been described in detail elsewhere.<sup>1</sup>

It was found that either a 2 per cent. solution of nitric acid in alcohol or a 5 per cent. picric acid in alcohol developed the structure in a very satisfactory manner.

To observe the general changes which take place a power of 44–88 diameters is used in an ordinary microscope in conjunction with a Sorby-Beck illuminator.<sup>1</sup> Then for more detailed work a higher magnification of 260–500 diameters was obtained by using a LeChatelier stand. Over 100 photographs were taken to record the various changes which take place. By choosing types, however, these have been represented by Figs. 14 to 25.

*Structure of the Original Steels as Rolled.*—Steel 1 consisted of

<sup>1</sup> Stead: Cleveland Inst. Engineers, February 26, 1900; Campbell: School of Mines Quart. 25, 390.

both patches and veins of cementite in a groundmass of pearlite, much of which is in the sorbitic condition. In a longitudinal section the patches of cementite are drawn out, while at the edge of the specimen the pearlite grain with its cementite envelope is elongated in the direction of rolling. Hence we may judge that rolling was finished after the cementite had begun to separate out, *i. e.*, in region of  $Ar_{2-3}$ . The comparatively rapid cooling of bars of  $\frac{5}{16}$  inch cross-section would produce pearlite in the sorbitic or unsegregated condition.

Steel 2 is similar but contains fewer patches of cementite.

Steel 3 consists of medium-sized grains of pearlite surrounded by irregular envelopes of cementite, and practically no patches as occur in Nos. 1 and 2. The pearlite varies from well-laminated to sorbitic.

Steel 4 shown in Fig. 14  $\times 260$  has a structure similar to steel 3.

Steel 5 as rolled consists of pearlite alone in medium-sized grains, whose texture varies from very fine to coarse.

Steel 6 shows some ferrite at the surface. The rest of the section consists of medium-sized grains of pearlite with very thin films of ferrite which disappear towards the center. Much of the pearlite is sorbitic.

As in the case of the physical properties and fractures the steels naturally fall into two groups, (1) steels 1 to 4 and (2) steels 5 and 6, according to their carbon content.

*Changes of Structure in Steels 1 to 4.*—Such heat treatment as the steels have undergone produces more or less decarburization. This first shows in heat 6,  $760^{\circ}$ , becomes more visible in the heat to  $800^{\circ}$  and probably gives the crystalline border to the fracture, while at  $1200^{\circ}$  it has penetrated deep into the steel. This is shown in Fig. 17  $\times 44$ , which is taken from the corner of steel 1 heat Z,  $1070^{\circ}$ . On the left-hand side we see the normal structure, globular cementite in pearlite, while the center of the photograph consists of pearlite alone, 0.9 per cent. carbon. At the extreme right ferrite makes its appearance at the corner of the specimen and the carbon content falls below 0.4 per cent. The same change through decarburization occurs in steels 5 and 6.

*Change in the Pearlite.*—In the bars as rolled the pearlite is either very finely laminated or in the sorbitic condition. Heating to even  $650^{\circ}$  causes a change and the pearlite tends to become granular, the cementite drawing up into globules which polish

in relief. The higher the temperature up to the critical point the stronger the segregation of the cementite of the pearlite. The size of grain of the pearlite, however, does not show any apparent change, until the critical point  $Ac_1$  is passed, when the steel is refined as regards the pearlite. Heating to temperatures above this point produces larger and larger grains of coarser and coarser pearlite. The coarseness depends on the rate of passing through  $Ar_1$  which was comparatively slow in these experiments. The size of grain as rolled is given in Fig. 14  $\times 260$ . That of steel No. 3 heated to  $1200^\circ$  is given in Fig. 23  $\times 44$  diameters only, and is over ten times as great.

*Change in the Cementite.*—As rolled the cementite occurs as veins or patches more or less drawn out in the direction of rolling. Heating to  $650^\circ$  or above causes these veins to break down, due to the tendency for the cementite to take a globular form. The higher the temperature the greater the segregation. Fig. 15  $\times 260$  shows steel No. 3, heat 2 to  $800^\circ$ , while Fig. 16 shows steel No. 2, heat 5 to  $950^\circ$ , in which globules of cementite have become very coarse indeed. Figs. 14, 15 and 16 illustrate the complete change very well indeed; but as the temperature rises above the critical point  $Ac_1$  (therefore in all heats above  $760^\circ$ ) the cementite also tends to dissolve in the solid solution formed by the transformation of the pearlite (and called austenite, martensite, hardenite, etc.). On cooling down again all of this dissolved cementite separates out, as a rule on the undissolved grains of cementite but lacking these, around the grain of the solid solution as an envelope. Arnold,<sup>1</sup> on the other hand, maintains that cementite only dissolves in the solid solution (hardenite) when the temperature has become a little above  $900^\circ$  and on cooling falls out of solution completely at about  $900^\circ$ . He also "advances the proposition that the  $Fe_3C$  of cementite and the  $Fe_3C$  of pearlite are physically different substances though identical in chemical composition."

As the temperature rises a point is reached where any cementite which remains undissolved breaks down into ferrite and graphite. As a rule we find a kernel of graphite with a skin of ferrite, but this latter may dissolve in the solid solution. Fig. 18  $\times 260$  shows the center of steel No. 1, heat 8 to  $1200^\circ$ , while Fig. 20 shows steel No. 2, same heat, from near the side. These sections show only ferrite

<sup>1</sup> Arnold : J. Iron and Steel Inst. 1899, 1, p. 85 ; 1905, 2, 27.

and graphite in a groundmass of pearlite and little or no cementite has been dissolved. Outside this graphite zone, however, the cementite has all dissolved and on cooling has separated as seen in Figs. 19 and 21. Fig. 19 $\times$ 260 shows outer zone of steel No. 2, heat 8 to 1200°, and Fig. 21 $\times$ 44 shows outer zone of steel No. 1, same heat, in which all of the cementite has separated out as veins and as sheets within the very coarse grain of the pearlite. This zone lies between the central core and the outside decarburized covering, and seems to show the beginning of the next change.

In the case of steels 3 and 4 the change of cementite into ferrite-graphite kernels occurs at 1070° or lower. When these steels are heated up to 1200° the whole of the cementite is taken into solution and separates out again on cooling as is shown in Figs. 23, 24 and 25. Fig. 23 $\times$ 44 diameters shows steel 3 heated to 1200° and slowly cooled, consisting of very coarse grains of pearlite surrounded by irregular envelopes of cementite, some of which has separated out within the grain as is characteristic of overheated material. (Fig. 24 $\times$ 44 oblique illumination shows up the change in color by changing the light from vertical to oblique, and now the pearlite appears light and the cementite dark.) Fig. 25 $\times$ 44 shows steel No. 4 heated to 1200° which is similar to the last but has a much smaller grain. The wavy irregular appearance of the cementite is well shown in Fig. 22 $\times$ 260 steel No. 3 heated to 1200°. The photo is taken from near the edge of the specimen.

To sum up, we find two changes taking place. The first occurs at a constant temperature, the change  $A_{c1}$  the transformation of the pearlite. The second is the change in the cementite. Heating causes the cementite to segregate, the higher the temperature the greater the segregation. At a certain temperature which differs in the different steels this segregated cementite breaks down into ferrite and graphite.<sup>1</sup> In steel No. 1 this occurs at 1200°, began at 950°, was marked at 1070° and complete at 1200° in steel No. 2. In steel No. 3 it was complete at 1070° while in steel No. 4, though not showing at 950°, the 1070° heat shows it together with the next change. Lastly, we have the complete solution of the cementite, the temperature of which also varies. In steels Nos. 1 and 2 this occurs above 1200°, in steels Nos. 3 and 4 it occurs at

<sup>1</sup> According to Arnold and McWilliam (J. I. S. I. 1905, 2, p. 47), this change takes place on cooling and occurs at a low red heat.



1200°, though steel No. 4 shows it beginning at 1070°. This dissolved cementite separates out on cooling as an irregular envelope to the pearlite grains.

These changes are of the utmost importance in the making of malleable castings, as well as in the manufacture of cutlery, etc. It must be added here that in different parts of bars of steels Nos. 1 and 2 as rolled traces of graphite were found in the center, and evidently formed during the rolling. These persist and are found in the 1070° heat, but for the sake of clearness they have not been considered here.

*Change of Structure in Steels 5 and 6.*—The changes which take place in the pearlite by heating up to the critical point are the same as described above.

*Steel 5, C=1.04.*—Heating to 800° causes a growth in the pearlite grain and allows the cementite in excess of the eutectoid ratio (0.9 per cent. carbon) to separate out as a thin film round the pearlite grain. Heating to 855° so coarsens the pearlite that the steel is overheated. The cementite film has disappeared.

*Steel 6, C=0.70 per cent.*—Heating up to the critical point in places produces a marked segregation of the cementite of the pearlite resulting in coarse lamination. Heating to 800° causes a great increase in grain size and the film of ferrite, seen in the section as rolled, has now changed to grains. The steel is overheated at this low temperature.

*Effect of Heat Treatment upon the Structure and Its Bearing on the Mechanical Properties.*—From the above work it is noted that heating to temperatures up to the critical point  $Ac_1$  in general, increases the ductility at the expense of the strength. The fractures show no marked change in size of grain till the critical point is reached, though of course they decrease in area. Under the microscope this is explained by (1) the breaking down of the veins of cementite and its segregation, tending to take a globular form and (2) a change in the character of the pearlite. The size of grain of the pearlite does not change until the critical point has been passed and it is therefore necessary to heat to a point just above  $Ac_1$  for complete refining.

In the case of the steels high in carbon (1 to 4) the strength, as compared with that of the refined bars, is changed but little on heating to higher temperatures, until at the maximum tem-

Steel No.	Temp. 1200°	1070°	950°	905°	855°	800°	760°	715°	650°	As rolled	Per cent carbon
6											0.70
5											1.04
4											1.61
3											1.72
2											1.94
1											2.04
	8	Z	5	0	4	2	6	1	3	A	Heat 1

Fig 1



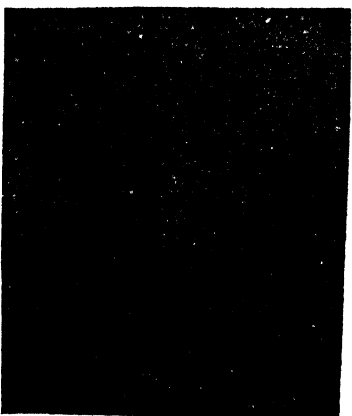


Fig. 2. Steel 2, heat 9050.

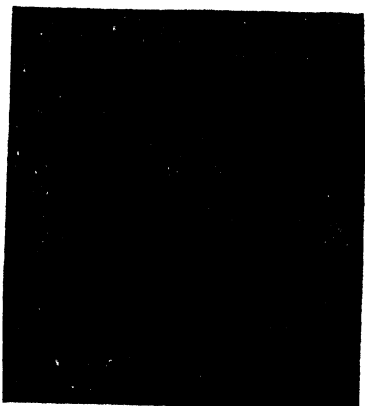


Fig. 3. Steel 2, heat 9300

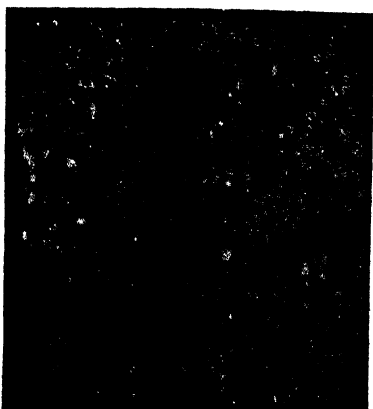


Fig. 4. Steel 2, heat 10700

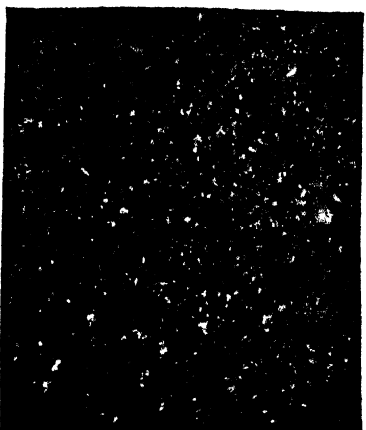


Fig. 5. Steel 2, heat 12000.

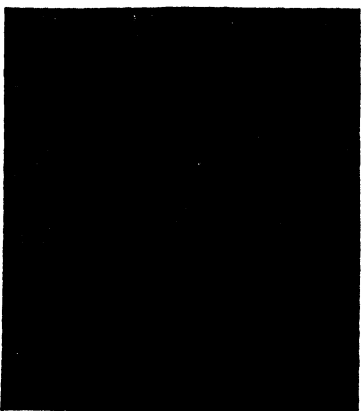


Fig. 6. Steel 3, as rolled

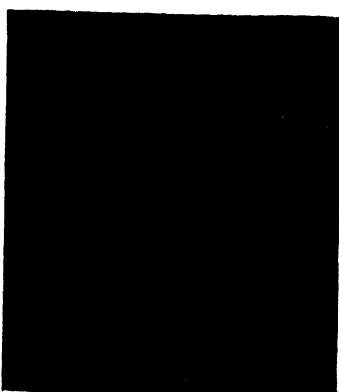


Fig. 7. Steel 3, heat 7150.



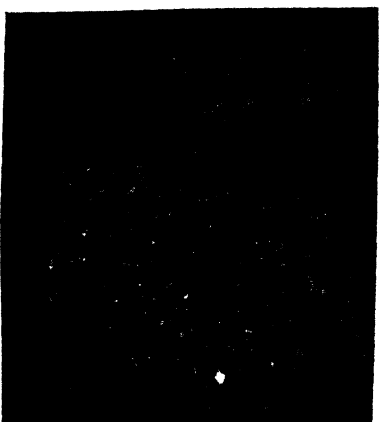


Fig 8 Steel 3 heat 1070°

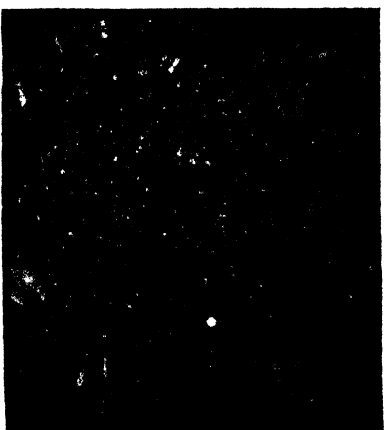


Fig 9 Steel 3 heat 1200°

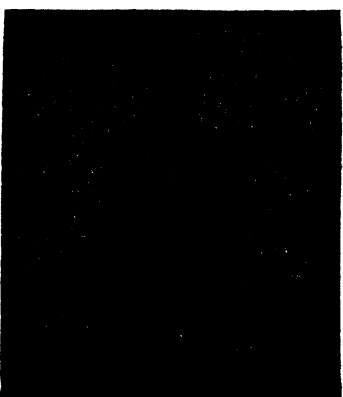


Fig 10 Steel 5, as rolled

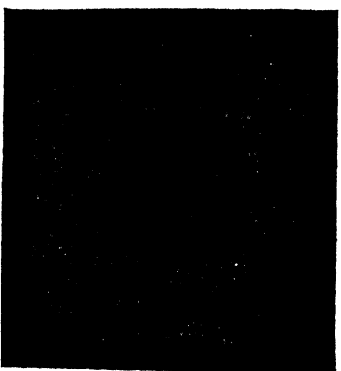


Fig 11 Steel 5, heat 650°.

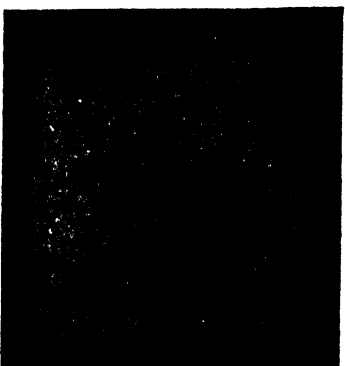


Fig 12 Steel 5 heat 715°

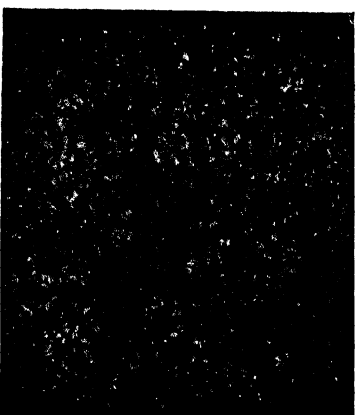


Fig 13 Steel 5, heat 1070°



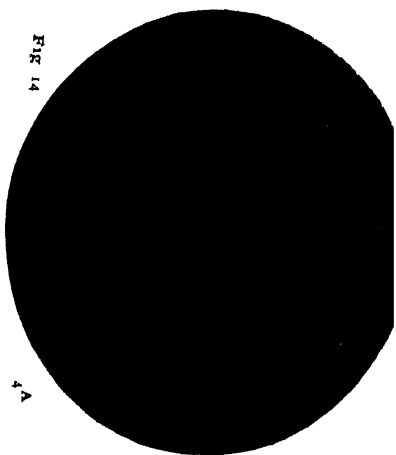


FIG 14

4A

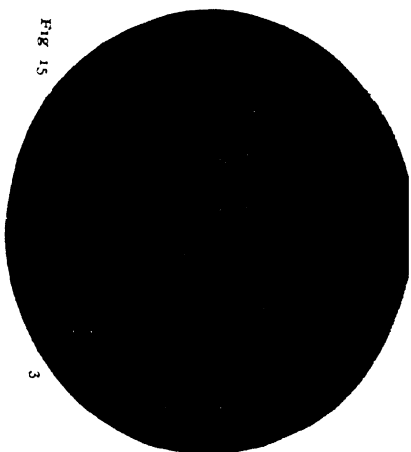


FIG 15

3

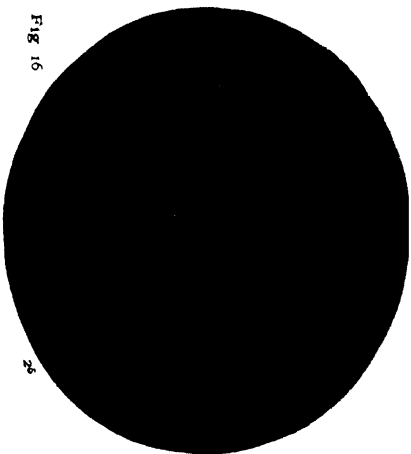


FIG 16

25

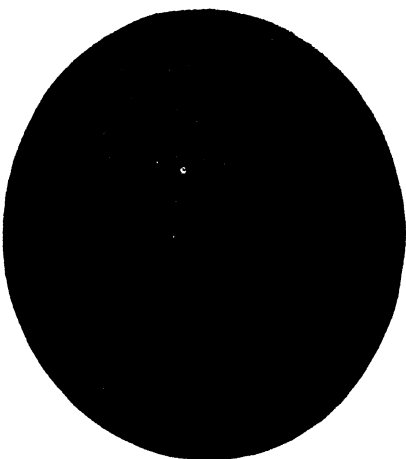


FIG 17

12

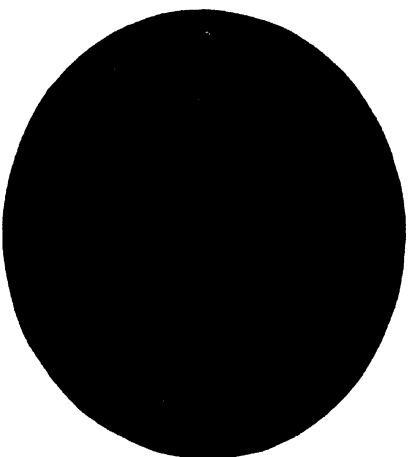


FIG 18

14

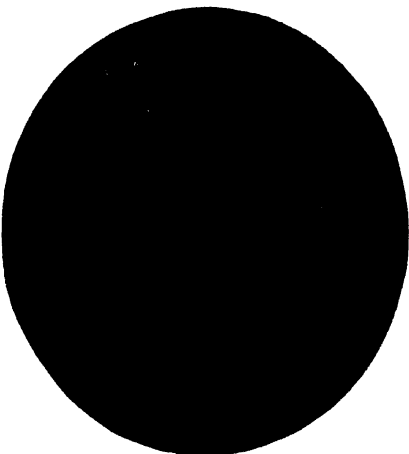


FIG 19

28





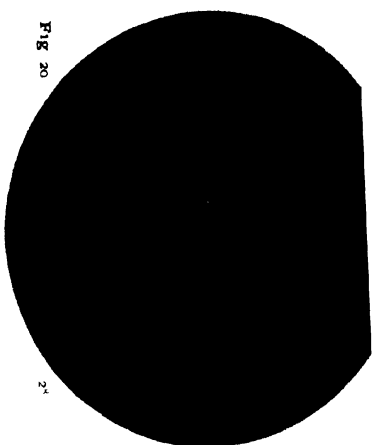


Fig. 20

2x

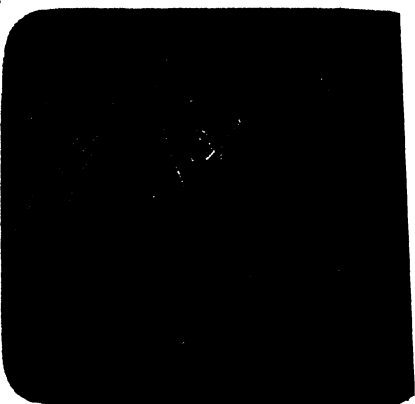


Fig. 21

1x

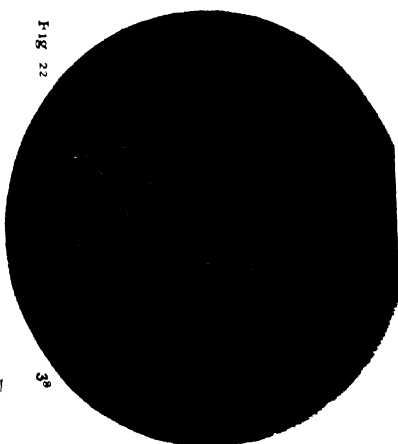


Fig. 22

3x



Fig. 23

3x

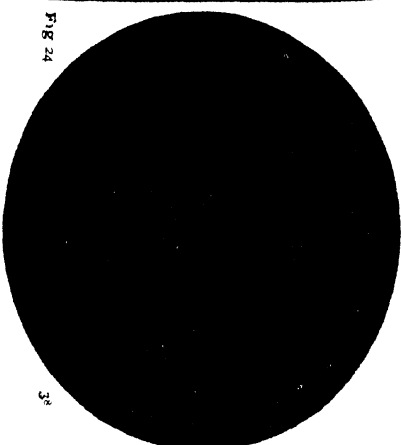


Fig. 24

3x

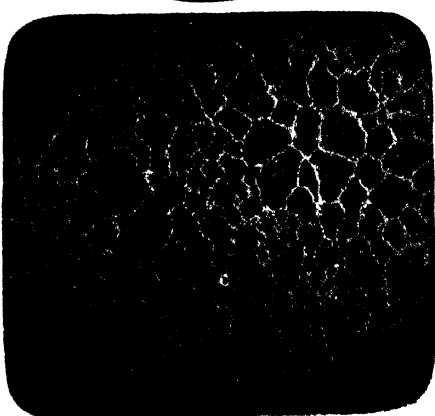


Fig. 25

4x



perature,  $1200^{\circ}$ , the maximum load takes a sudden drop and we have great overheating. The ductility on the other hand shows a steady fall to almost nil. An examination of the fractures shows a steady increase in size of grain up to  $1070^{\circ}$  at which point they suddenly become exceedingly coarse and show graphite. The microstructure shows a steady increase in the size of grains of the pearlite and of the segregation of the cementite. At the  $1070^{\circ}$  heat we see the breaking down of the segregated cementite into ferrite and graphite, with a great coarsening of the pearlite. In steels Nos. 3 and 4 the maximum heat,  $1200^{\circ}$ , produces another change, whereby the whole of the cementite is taken into solution resulting in a coarse network of cementite round large grains of pearlite. Such a structure accounts for the falling off in strength and ductility, while in the case of steels Nos. 1 and 2 this fall is apparently due to extreme coarseness of grain.

In the case of the steels low in carbon heating to temperatures above the critical point increases the strength compared with that of the refined bars. On the other hand, the ductility falls off. The fractures show that a temperature of  $855^{\circ}$  overheated steel No. 5, while  $800^{\circ}$  overheated steel No. 6, both of which are comparatively low temperatures. The microstructure shows that the pearlite has become coarse in grain and texture at these points, but it hardly accounts for the marked overheating at so low a temperature.

Thus we see that for each change in microstructure there is a corresponding change in mechanical properties and in fracture. So close are these relations that with little practice the latter can be predicted with certainty from the former.

*Conclusion.*—The above work is preliminary to a study of another series of six high carbon steels ranging in equal steps from 1 to 2 per cent. carbon and of larger cross-section, whereby it is hoped to work out definitely the change in steel of cementite = ferrite + graphite.

In conclusion I wish to acknowledge my indebtedness to the Carnegie Institution of Washington for a grant to carry on the work. I have also to thank Professor Howe and other friends for encouragement and advice.

## LIST OF ILLUSTRATIONS.

Fig. 1.—Assembled fractures of test-pieces.

Figs. 2 to 13.—Fractures  $\times 6$  diameters.

Fig. 2.—Steel 2. C = 1.94 per cent. Heat o. 905° C.  
 Fig. 3.— “ 2. C = 1.94 “ “ 5. 950° C.  
 Fig. 4.— “ 2. C = 1.94 “ “ Z. 1070° C.  
 Fig. 5.— “ 2. C = 1.94 “ “ 8. 1200° C.  
 Fig. 6.— “ 3. C = 1.72 “ As rolled.  
 Fig. 7.— “ 3. C = 1.72 “ Heat 1. 715° C.  
 Fig. 8.— “ 3. C = 1.72 “ “ Z. 1070° C.  
 Fig. 9.— “ 3. C = 1.72 “ “ 8. 1200° C.  
 Fig. 10.— “ 5. C = 1.04 “ As rolled.  
 Fig. 11.— “ 5. C = 1.04 “ Heat 6. 650° C.  
 Fig. 12.— “ 5. C = 1.04 “ “ 1. 715° C.  
 Fig. 13.— “ 5. C = 1.04 “ “ Z. 1070° C.

Fig. 14.—25.—Microstructure.

Fig. 14.— “ 4. C = 1.61 “ As rolled  $\times 260$ .  
 Fig. 15.— “ 3. C = 1.72 “ Heat 2. 800° C.  $\times 260$ .  
 Fig. 16.— “ 2. C = 1.94 “ “ 5. 950° C.  $\times 260$ .  
 Fig. 17.— “ 1. C = 2.04 “ “ Z. 1070° C. Corner  $\times 44$ .  
 Fig. 18.— “ 1. C = 2.04 “ “ 8. 1200° C. Center  $\times 260$ .  
 Fig. 19.— “ 2. C = 1.94 “ “ 8. 1200° C. Between center  
 and outside  $\times 200$ .  
 Fig. 20.— “ 2. C = 1.94 “ “ 8. 1200° C. Near center of  
 side  $\times 60$ .  
 Fig. 21.— “ 1. C = 2.04 “ “ 8. 1200° C. Between center  
 and outside  $\times 44$ .  
 Fig. 22.— “ 3. C = 1.72 “ “ 8. 1200° C. Near outside  $\times$   
 260.  
 Fig. 23.— “ 3. C = 1.72 “ “ 8. 1200° C. Center  $\times 44$ .  
 Fig. 24.—The same, oblique illumination.  
 Fig. 25.—Steel 4. C = 1.61 per cent. Heat 8. 1200° C. Near center  $\times$   
 44.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COL-  
 LEGE.]

## A REVISION OF THE ATOMIC WEIGHT OF BROMINE.

BY GREGORY PAUL BAXTER.

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In numerous investigations in this laboratory upon the atomic weights of certain metals, in which metallic bromides were first titrated against the purest silver, and then the precipitated silver bromide was collected and weighed, the relation between the silver used in the titrations and the silver bromide obtained has yielded

data from which the atomic weight of bromine may be calculated. Furthermore, in all these investigations, as a check upon the purity of the silver and bromine employed, silver bromide was synthesized directly from weighed quantities of silver and an excess of ammonium bromide or hydrobromic acid. Many of these results have already been collected and discussed by Richards;<sup>1</sup> nevertheless they are cited in the following table together with a few more recent determinations.

## INDIRECT DETERMINATIONS.

	Bromide analyzed.	Number of experiments.	Analyst.	Reference	Ratio. $\frac{\text{Ag}}{\text{AgBr}}$
1	BaBr <sub>2</sub>	Last seven	Richards	Pr. Am. Acad., 28, 28	57.444
2	SrBr <sub>2</sub>	Seven	"	Ibid., 30, 389	57.444
3	ZnBr <sub>2</sub>	One	"	Ibid., 31, 178	57.445
4	NiBr <sub>2</sub>	Seven	Cushman	Ibid., 33, 111	57.444
5	CoBr <sub>2</sub>	Last five	Baxter	Ibid., 33, 127	57.446
6	UBr <sub>4</sub>	Three	Merigold	Ibid., 37, 393	57.447
7	CsBr	Three	Archibald	Ibid., 38, 466	57.444
8	FeBr <sub>2</sub>	Two	Baxter	Ibid., 39, 252	57.443
9	CdBr <sub>2</sub>	Eight	Hines	This Journal, 28, 783	57.444
10	MnBr <sub>2</sub>	Thirteen	"	Not yet published	57.444

Average, weighted according to the number of determinations, 57.4443

## DIRECT DETERMINATIONS.

11	HBr	Two	Richards	Pr. Am. Acad., 28, 17, 18	57.445
12	NH <sub>4</sub> Br	One	"	Ibid., 30, 380	57.446
13	HBr	Two	"	Ibid., 31, 165	57.444
14	NH <sub>4</sub> Br	One	Cushman	Ibid., 33, 106	57.445
15	NH <sub>4</sub> Br	One	Baxter	Ibid., 33, 122	57.444
16	NH <sub>4</sub> Br	Two	"	Ibid., 34, 353	57.447
17	NH <sub>4</sub> Br	Three	"	Ibid., 39, 250	57.444
18	NH <sub>4</sub> Br	One	Hines	Not yet published	57.443

Average, weighted according to the number of determinations, 57.4447

From the first of these ratios the atomic weight of bromine, referred to silver 107.930, is found to be 79.956, and from the second 79.955.

Very recently, in experiments in which silver iodide was heated first in a current of air and bromine until the iodine was completely displaced, and then in a current of chlorine to displace the bromine, the ratio of silver bromide to silver chloride was determined in six cases. From the results of these experiments the atomic weight of bromine was calculated to be 79.953,<sup>2</sup> if the

<sup>1</sup> Pr. Am. Phil. Soc. 43, 119 (1904).

<sup>2</sup> Baxter: This Journal, 27, 884 (1905).

atomic weight of chlorine is assumed to be 35.473.<sup>1</sup>

These values for bromine are in close agreement with those of Stas.<sup>2</sup> In his experiments weighed quantities of pure silver and bromine were first titrated against each other, and then the precipitate of silver bromide was collected and weighed. Of the four results by the first method, one should be rejected according to his own statements, since the bromine was not thoroughly dried. The remaining three, 79.959, 79.961 and 79.960, give as an average 79.960. From the weight of silver bromide four values were obtained, 79.950, 79.952, 79.955 and 79.957, with an average of 79.954.

Marignac<sup>3</sup> also determined the ratio of silver to silver bromide, with somewhat lower results—79.959, 79.941 and 79.952; average, 79.950.

Scott,<sup>4</sup> in his analyses of ammonium bromide, obtained six values for the same ratio, varying between 79.936 and 79.948, with an average of 79.943. One of his results is here rejected, since the silver used in this experiment was known to be impure.

Dumas,<sup>5</sup> by heating silver bromide in chlorine, found the values 80.06, 79.89 and 79.96.

In computing the atomic weight of bromine from these data, great weight is always given to Stas's determinations, the value 79.955 being usually assumed as the most probable one for the constant in question. Certainly, as pointed out by Richards,<sup>6</sup> the true value must lie between 79.95 and 79.96. Clarke calculates the value 79.949 as the weighted average of the different investigations previous to Scott's.<sup>7</sup>

Considerable uncertainty exists as to the purity of the materials employed in much of the foregoing work. Richards and Wells<sup>8</sup> have already exhaustively investigated the various methods of preparing pure silver, and have found that while it is a comparatively simple matter to free this substance from metallic

<sup>1</sup> Richards and Wells: Publications of the Carnegie Institution, No. 28 (1905); This Journal, 27, 459.

<sup>2</sup> Œuvres Complètes. 1, 603.

<sup>3</sup> Ibid. 1, 81.

<sup>4</sup> J. Chem. Soc. 79, 147 (1901).

<sup>5</sup> Ann. Chem. Pharm. 113, 20 (1860).

<sup>6</sup> Pr. Am. Phil. Soc. 43, 119 (1904).

<sup>7</sup> "A Recalculation of Atomic Weights," Smith. Misc. Coll., 1897.

<sup>8</sup> Publications of the Carnegie Institution, No. 28, 16; also this Journal, 27, 472 (1905).

impurities, the absence of gaseous impurities is by no means so easy to secure. Oxygen may be eliminated best by fusion in an atmosphere of pure hydrogen gas,<sup>1</sup> or by prolonged fusion in a vacuum, while a lime boat was found to be the most suitable support for the silver during fusion.

In most of the experiments cited on page 202, one of the final steps in the purification of the silver was fusion of electrolytic crystals on lime, in many cases in a vacuum, but without especial care to prolong the fusion. Silver prepared in this way was found by Richards and Wells to contain traces of oxygen, derived from silver nitrate occluded by the electrolytic crystals. In cases 8, 9, 10, 17 and 18, however, the silver was fused in hydrogen. Richards and Wells showed also that Stas's silver contained at least 0.01 per cent. of impurity, since it yielded 0.01 per cent. less silver chloride than their purest silver.<sup>2</sup> Scott's silver in three cases was merely heated, not fused, in hydrogen, and in two of the others was fused before a blowpipe on calcium phosphate. In one experiment only the metal was fused on lime. No details are given as to the purification of the silver used by Marignac.

Bromine also may be freed from impurities only with some difficulty. Experience in this laboratory has shown that chlorine may be eliminated most conveniently by distilling or precipitating the bromine from solution in a bromide. One such distillation is sufficient to remove chlorine completely only when the substance is initially comparatively pure. If, however, the process is repeated by converting a portion of the partially purified product into a bromide, and dissolving the remainder of the bromine in this comparatively pure bromide, the chlorine is eliminated so completely that further repetitions of this process have no apparent effect.<sup>3</sup> The removal of iodine may be easily effected by converting the bromine into hydrobromic acid or a soluble bromide, and boiling the solution with a small quantity of free bromine. Here again it is well to repeat the process several times, since the reaction between free bromine and the iodine ion, like that between free chlorine and the bromine ion, is undoubtedly incomplete.

<sup>1</sup> Baxter : *Pr. Am. Acad. Arts Sci.* 39, 249 (1903).

<sup>2</sup> *Loc. cit.*, page 62.

<sup>3</sup> Attention has already been called to these points by Richards and Wells : *Pr. Am. Acad. Arts Sci.*, 41, 440 (1906).



The greater part of the experiments cited on page 1323 were made with bromine which had been purified with due observance of these precautions. Of the other investigators, Stas seems to have been the only one to use sufficient pains to secure purity of the bromine. Stas removed iodine by shaking potassium bromide several times with free bromine and carbon disulphide, and in the course of the prolonged purification distilled the bromine twice from solution in a bromide. Marignac's purification consisted solely in crystallization of barium bromate and Scott's in distillation of hydrobromic acid.

Of the methods employed in these early determinations, that involving the analysis of metallic halides is least suited for the purpose, on account of the danger of occlusion of metallic salts by the precipitated silver bromide. That such an error actually exists to a slight extent is shown by the fact that the average of the "indirect" determinations is slightly larger than the average of the "direct" determinations. Obviously, if silver bromide is precipitated by means of either ammonium bromide or hydrobromic acid, occluded ammonium salts or free acids could be easily expelled by fusion of the bromide. This precaution was observed in most of the determinations recorded on page 202, and is absolutely essential for the complete elimination of water from the salt. Stas and Marignac both fused the silver bromide in their syntheses, but this precaution was omitted by Scott, who dried the bromide at  $180^{\circ}$ . Scott's statement that the loss on fusion of silver bromide which had been dried at  $180^{\circ}$  was due to the presence of asbestos is contradicted by the experiments recorded later in this paper, in which the loss on fusion amounted to about 0.01 per cent. in the case of silver bromide which had been dried in a similar fashion and which was almost entirely free from asbestos.

From this brief discussion of the more important errors which may have influenced previous determinations of the atomic weight of bromine, it is evident that some uncertainty still exists as to the true value of this constant. In the hope of throwing new light upon the subject, experiments were carried out by two of the methods outlined above, with especial precautions to insure purity of materials and to eliminate known possible errors in the experimental methods.

Both the methods chosen—synthesis of silver bromide from a weighed amount of silver, and conversion of silver bromide into

silver chloride—have already been recently tested in this laboratory,<sup>1</sup> and have been found to be at least as satisfactory as any.

#### PURIFICATION OF MATERIALS.

*Bromine.*—In purifying bromine for this research, the principles set forth on page 1325 of this paper were applied, but in some cases the purifying processes were repeated after the product was apparently pure, in order to make certain that further treatment had no effect.

Sample I was first completely dissolved in calcium bromide which had been made from about one-third of the original material by means of lime and ammonia, and was then distilled from the solution. The product was covered with several times its volume of water, and was converted into hydrobromic acid by means of pure hydrogen sulphide which had been generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtration from the precipitated sulphur and bromide of sulphur, the acid was boiled for some time, with occasional addition of small quantities of recrystallized potassium permanganate to eliminate the iodine. Finally, the residual hydrobromic acid was heated with an equivalent amount of recrystallized permanganate, and the bromine was condensed in a flask cooled with ice.

Sample II was first converted into hydrobromic acid by means of red phosphorus and water, and the hydrobromic acid was then distilled, after having been boiled with an excess of bromine. An equivalent amount of permanganate was added, and the bromine liberated was separated from the solution by distillation. About one-fourth of the product was next transformed into calcium bromide by means of ammonia and lime which was free from chloride, and the remaining three-fourths of the bromine were dissolved in the calcium bromide and distilled. Still a third distillation from a bromide was carried out by reducing the product of the second distillation with hydrogen sulphide and subsequently oxidizing the hydrobromic acid with the purest recrystallized potassium permanganate, after boiling the acid with several small portions of permanganate to eliminate the last traces of iodine.

Sample III was obtained by preparing calcium bromide from a

<sup>1</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 419; 41, 73. Richards and Wells: *Publications of the Carnegie Institution*, No. 28; *This Journal*, 27, 876 (1905).

portion of Sample II and distilling the remainder of Sample II from solution in this bromide.

In the case of Sample IV the processes of reduction to hydrobromic acid with hydrogen sulphide and oxidation of the hydrobromic acid with pure permanganate were four times repeated. After each reduction the hydrobromic acid was boiled with free bromine to remove iodine.

Sample V was three times reduced with hydrogen sulphide and oxidized with permanganate. One-fourth the product was converted into calcium bromide and the remainder was dissolved in this calcium bromide and distilled.

Thus Sample I was twice distilled from a bromide; Sample II was treated three times in the same way; and Samples III, IV and V four times.

Shortly before use each sample was distilled and converted into ammonium bromide by slow addition to an excess of redistilled ammonium hydroxide. The solution was then boiled to expel the excess of ammonia.

*Silver.*—Several different samples of silver were employed, many of which have already been used in atomic weight researches in this laboratory, and have shown evidence of great purity. For details concerning the purification the papers referred to should be consulted.

Sample A was employed in a determination of the atomic weight of iodine.<sup>1</sup> This specimen had been twice precipitated as chloride and once electrolyzed.

Sample B was used in experiments upon the atomic weight of iodine<sup>2</sup> and of manganese.<sup>3</sup> It was precipitated once as chloride, electrolyzed once, and finally precipitated as metal with ammonium formate.

Sample C also was employed in a determination of the atomic weight of manganese, and was purified by recrystallizing silver nitrate, seven times from nitric acid and five times from aqueous solution. Finally, the silver nitrate was reduced by means of ammonium formate.

Sample D was prepared for the determination of the atomic

<sup>1</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 420 (1904); *This Journal*, 27, 381 (1905).

<sup>2</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 41, 79 (1905); *This Journal*, 27, 381 (1905).

<sup>3</sup> Baxter and Hines: This paper will soon be published.

weights of cadmium<sup>1</sup> and manganese, by one precipitation as chloride, one precipitation with ammonium formate, and one electrolysis.

Sample E was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses.

In all cases the electrolytic crystals were fused in a boat of the purest lime, contained in a porcelain tube, in a current of electrolytic hydrogen. After the buttons had been cleansed with dilute nitric acid and dried at 200°, they were cut into fragments of from 4 to 8 grams either by means of a clean chisel and anvil or with a fine jeweler's saw. The latter method was employed in the case of Samples D and E, because it proved easier completely to free the silver from surface contamination with iron by etching the fragments with nitric acid, than when a chisel was used. The cleansing process with nitric acid was repeated until the solution thus obtained, after precipitation with hydrochloric acid and evaporation, proved free from iron. That every trace of iron could be removed by this treatment was proved by testing for iron the evaporated filtrates from several of the analyses subsequently recorded in this paper. Negative results were obtained in all cases.

After thorough washing with water and drying at 100°, the pieces of metal were heated to about 400° in a vacuum, and were preserved over solid potassium hydroxide in a desiccator.

#### THE RATIO OF SILVER TO SILVER BROMIDE.

The ratio of silver to silver bromide was determined as follows: Weighed quantities of silver were dissolved in the purest re-distilled nitric acid diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible splatterings. However, during the solution of the silver the temperature was kept so low that almost no gas was evolved, and hence there was very little danger from this source. Next the acid solution of the silver was diluted with an equal volume of water, and was heated until free from nitrous acid and oxides of nitrogen. After still further dilution, the solution was added slowly with constant agitation to a dilute solution of an excess of ammonium bromide in a glass-stoppered precipitating flask, and the whole was violently

<sup>1</sup> Baxter and Hines : This Journal, 28, 772 (1906).

shaken for some time to promote coagulation. By adding the silver solution to the bromide, occlusion of silver nitrate was almost wholly precluded. In some experiments the solutions were as dilute as twentieth-normal, in others as concentrated as fourth-normal. The final results seemed to be independent of the concentration of the solutions. At the end of about twenty-four hours the flask with its contents was again shaken, and then it was allowed to stand until the supernatant liquid was perfectly clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after thorough washing by decantation with water, and was dried in an electric oven, first for several hours at  $130^{\circ}$ , finally for about fourteen hours at  $180^{\circ}$ . Then it was cooled and weighed.

The operations of precipitation and filtration were performed in a large cupboard lighted with red light, and if the flask was taken out of this cupboard it was enveloped in several thicknesses of black cloth.

Even after the prolonged drying, traces of moisture were retained by the salt, and could be expelled only by fusion. This was done by transferring the bulk of the silver bromide, freed as completely as possible from asbestos, to a small porcelain crucible which was weighed with its cover. The silver bromide was then fused by heating the small crucible, contained in a large crucible to prevent direct contact with the flame of the burner. A temperature much above the fusing point of silver bromide was avoided so that volatilization of the salt could not take place. This treatment must have eliminated occluded ammonium salts as well as water. Finally, in order to convert any occluded silver nitrate, metallic silver, or silver sub-bromide into silver bromide, the salt was again fused in a current of dry air containing bromine vapor. This treatment seldom produced any measurable effect either upon the weight or the appearance of the salt, which was perfectly transparent and of a light yellow color even after the first fusion in air.

A few shreds of asbestos displaced from the crucible, together with an occasional trace of silver bromide which escaped the crucible, were collected upon a tiny filter-paper which was then ignited in a porcelain crucible. Before being weighed the ash was either treated with a drop of nitric and hydrobromic acids

and again heated, or else was heated for some minutes in a current of air and bromine.

The filtrate and washings were evaporated to small bulk. The precipitating flask and all other glass vessels used in the analysis were rinsed with ammonia and the rinsings were added to the evaporated filtrate and wash-waters. The whole was then tested in a nephelometer for silver and the quantity found was estimated by comparison with standard silver solutions. In most cases the correction thus obtained was less than 0.1 mg.

The asbestos which formed the felt in the Gooch crucible, after having been shredded, was digested for some hours with aqua regia and was then thoroughly washed with water. Before the empty crucible was weighed, the felt was ignited with a Bunsen burner. Crucibles thus treated and then heated to  $180^{\circ}$  after being moistened with water did not change in weight.

In the following table are cited all the analyses which were completed without accident. Vacuum corrections of  $-0.000031$  for every apparent gram of silver and of  $+0.000041$  for every apparent gram of silver bromide are applied.<sup>1</sup> The atomic weight of silver is assumed to be 107.930.

The platinum plated brass weights were standardized from time to time and were found to retain their original values within a very few hundredths of a milligram in all cases.

#### THE RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

The ratio of silver bromide to silver chloride was determined much as described in previous papers upon the atomic weight of iodine.<sup>2</sup> Pure silver bromide was prepared by precipitation of silver nitrate with an excess of ammonium bromide. The silver employed was purified either by precipitation as chloride and reduction with invert sugar, or by electrolysis, or by precipitation with ammonium formate. The metal was then fused before a blowpipe upon a crucible of the purest lime, and the buttons were thoroughly cleansed with nitric acid. No further purifica-

<sup>1</sup> The specific gravity of the weights was determined to be 8.3. The specific gravity of silver has been found to be 10.49. Richards and Wells: Publications of the Carnegie Institution, No. 28, 11. The specific gravity of fused silver bromide has been found to be 6.473. Baxter and Hines: *Am. Ch. J.* 31, 224.

<sup>2</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 432 (1904); 41, 75 (1905); *This Journal*, 27, 876 (1905).

TABLE I.—THE ATOMIC WEIGHT OF BROMINE. SERIES I.

Number of analyses.	Sample of silver.	Sample of bromine.	Ag : AgBr.		Loss on fusion in bromine.	Weight of silver ver bromide in vacuum.	Ag : AgBr.		Weight of asbestos.	Ag = 107.930		Corrected wt. of silver bromide.	Ratio Ag : AgBr	Atomic weight of bromine.
			Grams.	Grams.	Grams.	Grams.	Grams.	Grams.		Grams.	Grams.			
1	A	II	4.71853	8.21362	0.00027	0.00007	0.00021	8.21363	57.4476	79.946				
2	B	II	5.01725	8.73387	0.00020	0.00019	0.00007	8.73393	57.4455	79.952				
3	A	II	5.96818	10.38799	0.00023	0.00034	0.00122	10.38932	57.4453	79.953				
4	C	II	5.62992	9.80000	0.00017	0.00039	0.00017	9.80039	57.4459	79.951				
								Average,	57.4461	79.950				
5	A	IV	8.13612	14.16265	0.00002	0.00047	0.00024	14.16334	57.4449	79.954				
6	C	IV	5.07238	8.82932	0.00013	0.00043	0.00035	8.82997	57.4451	79.954				
7	B	IV	4.80711	8.36838	0.00015 <sup>1</sup>	0.00000	0.00004	8.36827	57.4445	79.956				
								Average,	57.4448	79.955				
8	C	V	4.27279	7.43771	0.00010 <sup>1</sup>	0.00009	0.00007	7.43776	57.4473	79.947				
9	A	V	5.86115	10.20299	0.00007 <sup>1</sup>	0.00004	0.00003	10.20299	57.4454	79.953				
10	B	V	7.91425	13.77735	0.00010	0.00010	0.00001	13.77736	57.4439	79.958				
11	D	V	6.40765	11.15461	0.00000	0.00006	0.00001	11.15468	57.4436	79.959				
12	D	V	6.38180	11.10942	0.00025	0.00012	0.00001	11.10930	57.4456	79.952				
13	D	V	6.23696	10.85722	0.00005	0.00004	0.00001	10.85722	57.4453	79.953				
								Average,	57.4452	79.953				
14	E	I	9.18778	15.99383	0.00014	0.00019	0.00004	15.99392	57.4455	79.953				
15	E	I	8.01261	13.94828	0.00018	0.00009	0.00007	13.94826	57.4452	79.953				
16	E	I	10.48638	18.25467	0.00025 <sup>1</sup>	0.00007	0.00001	18.25452	57.4454	79.953				
								Average,	57.4454	79.953				
17	E	III	8.59260	14.95790	0.00014	0.00016	0.00005	14.95797	57.4450	79.954				
18	E	III	8.97307	15.62013	0.00004	0.00007	0.00006	15.62022	57.4452	79.953				
								Average,	57.4451	79.954				
	Total,		121.67653					211.81305	57.4452	79.953				
								Average of all 18 determinations,	57.4453	79.953				
								Average of last 7 determinations,	57.4453	79.953				

<sup>1</sup> Fusion in bromine lost, after the salt had been fused in air.

tion was considered necessary, since the weight of the metal was of no consequence.

After the silver bromide had been washed by decantation with water, in some cases it was collected in a Gooch crucible in which a disk of filter-paper was employed instead of asbestos, and after drying at  $100^{\circ}$  it was carefully separated from the filter-paper. In other cases the precipitate was transferred to a platinum dish, and was drained with a platinum reverse filter<sup>1</sup> with a disk of filter-paper. In still others a platinum Gooch crucible with small holes was found to be sufficiently effective as a filtering medium without the use of either asbestos or filter-paper.

Before being weighed the silver bromide was fused in a current of air saturated with bromine in a weighed quartz crucible. The air was purified by passing successively over beads moistened with silver nitrate solution, over sodium carbonate, and finally over concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. The air was then passed through dry bromine in a small bulb. This apparatus was constructed entirely of glass with ground joints. The tube which conducted the gases into the crucible passed through a Rose crucible cover of glazed porcelain in all experiments except analyses 28 to 31, in which a quartz cover was employed. The quartz crucibles were always contained in large porcelain crucibles while being heated. They remained almost absolutely constant in weight during the experiments. The bromine was in each case a portion of the sample from which the silver bromide had been made.

Next the bromide was heated barely to fusion in a slow current of chlorine, generated by the action of hydrochloric acid upon manganese dioxide, and dried by means of concentrated sulphuric acid. The apparatus for this purpose also was constructed wholly of glass. When the bromine was apparently completely displaced, the silver chloride was heated in the air for a few minutes to expel dissolved chlorine, and then was cooled and weighed. A repetition of the heating in chlorine seldom affected the weight of the salt more than a few hundredths of a milligram, although occasionally a third heating was necessary to effect this result.

That no loss of silver chloride by volatilization took place is

<sup>1</sup> Cooke: *Pr. Am. Acad. Arts Sci.* 12, 121.



certain for two reasons. In the first place the cover of the crucible and the delivery tube for the bromine when rinsed with ammonia and the solution treated with a slight excess of hydrochloric acid gave no visible opalescence in the nephelometer. In the second place the weight of the chloride became constant without difficulty. It has already been shown that silver chloride which has been fused in chlorine, if subsequently heated in air, retains no excess of chlorine.<sup>1</sup>

The following vacuum corrections were applied: Silver bromide,  $+0.000041$ ; silver chloride,  $+0.000071$ .<sup>2</sup> The atomic weight of chlorine referred to silver 107.930 is assumed to be 35.473.

Aside from the close agreement of all the results of Series I, the fact is to be emphasized, that of the last seven analyses, which were consecutive, only two differ from the average of the series, 79.953, by as much as one one-thousandth of a unit. Furthermore, there is no evidence of any dissimilarity in the different preparations of bromine. Material which has received only two distillations from a bromide gives values no lower than bromine which has been thus treated four times. The various specimens of silver also show no difference in purity.

In the case of Series II, the extreme variation of the results is only four-thousandths of a unit, and only one of the thirteen experiments yielded a value which differs from the average by more than one one-thousandth of a unit.

Finally, the difference between the averages of Series I and II is only seven ten-thousandths of a unit. It is extremely unlikely that constant errors could have affected both series equally, so that this striking agreement is strong proof that both series are free from such errors.

It has already been pointed out that the average of Stas's syntheses, 79.954, probably represents with considerable accuracy the atomic weight of bromine, and that certainly his determinations are more accurate than those of later experimenters. His syntheses are few in number, however, and differ among themselves by several thousandths of a unit, so that they do not define within this amount the constant in question. Their average,

<sup>1</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 432 (1904); *This Journal*, 26, 1591 (1904); Richards and Wells: *Publications of the Carnegie Institution*, No. 28, page 59.

<sup>2</sup> Richards and Stull have found the density of fused silver chloride to be 5.56.

however, confirms the value obtained in this paper. From all the experiments here described the number 79.953 seems to be the most probable value for the atomic weight of bromine if the atomic weight of silver is assumed to be 107.930.

TABLE II.—THE ATOMIC WEIGHT OF BROMINE. SERIES II.

AgBr : AgCl.					
Ag = 107.930			Cl = 35.473.		
Number of analysis	Sample of bromine	Weight of silver bromide in vacuum Grams	Weight of silver chloride in vacuum Grams	Ratio $\frac{\text{AgBr}}{\text{AgCl}}$	Atomic weight of bromine.
19	II	8 03979	6 13642	131 0176	79.953
20	II	8 57738	6 54677	131 0170	79.952
21	II	13 15698	10 04221	131 0168	79 952
Average,				131 0171	79.952
22	IV	12.71403	9 70413	131 0167	79 952
23	IV	13 96784	10 66116	131.0162	79.951
Average,				131.0164	78.952
24	V	13 08168	9 98469	131.0174	76 953
25	V	12.52604	9 56059	131 0175	79.953
26	V	11.11984	8 48733	131 0170	79 952
27	V	8 82272	6 73402	131 0172	79 953
Average,				131 0173	79 953
28	I	11 93192	9 10721	131.0162	79.951
29	I	12 53547	9 56767	131.0190	79.955
Average,				131 0176	79.953
30	III	17 15021	13 09009	131.0167	79.952
31	III	10 31852	7 87572	131.0168	79 952
Average,				131.0168	79.952
Total,		153 94242	117 49801	131.0170	79.952
Average of all 13 experiments,				131.0171	79.952
Average of Series I and II,					79.953

In conclusion, attention may be called to the fact that a diminution in the atomic weight of bromine raises slightly all atomic weights resulting from the analysis of metallic bromides by precipitation with silver.

I am deeply indebted to the Carnegie Institution of Washington and to the Cyrus M. Warren Fund for Research in Harvard University for assistance in pursuing this investigation.

## THE SOLUBILITY OF POTASSIUM PERMANGANATE.

BY GREGORY P. BAXTER, ARTHUR C. BOYLSTON AND ROBERT A. HUBBARD.

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DETERMINATIONS of the solubility in water of potassium permanganate have been made by Mitscherlich,<sup>1</sup> who found 6.3 parts of salt to 100 parts of water in a saturated solution at 15°, by Guthrie,<sup>2</sup> who found 2.9 parts of salt to 100 parts of water at -0.6°, and by Muthmann and Kuntz,<sup>3</sup> who found 41.81 grams of permanganate dissolved in 1 liter of water at "about 7°." The data obtained in the present investigation cover the above range of temperature and extend as high as 65°.

Potassium permanganate for the determinations was purified by crystallization. The salt was first dissolved in the purest water and the solution was filtered through asbestos in a Gooch crucible without being allowed to come in contact with rubber. The solution was then evaporated in covered flasks to crystallization and the product was twice recrystallized, with centrifugal drainage. In all three crystallizations the hot solution was allowed to stand some time and was carefully decanted from possible sediment before cooling. All the water used in the purification and also in the analyses of the saturated solutions was twice distilled, once from an alkaline solution of permanganate and once from a trace of sulphuric acid. The final product, when dissolved in the purest water did not appreciably stain clean glass, and showed every outward evidence of purity.

The method of obtaining a saturated solution was the usual one of rotating the substance with water in closed tubes at the desired temperature in a thermostat. By means of electrical regulating apparatus the thermostat was maintained constant at different temperatures to within five hundredths of a degree. The thermometer was carefully corrected by comparison with one standardized by the Physikalisch-technische Reichsanstalt.

Since permanganates are easily reduced by rubber or cork, and since glass stoppers may become loose or may leak, the glass tubes,

<sup>1</sup> Pogg. Ann. 25, 295 (1832).

<sup>2</sup> Phil. Mag. [5] 6, 37 (1878).

<sup>3</sup> Z. Krist. Min. 23, 374 (1894).

2 cm. in diameter, in which the solutions were shaken, were sealed off after the permanganate and water had been introduced.

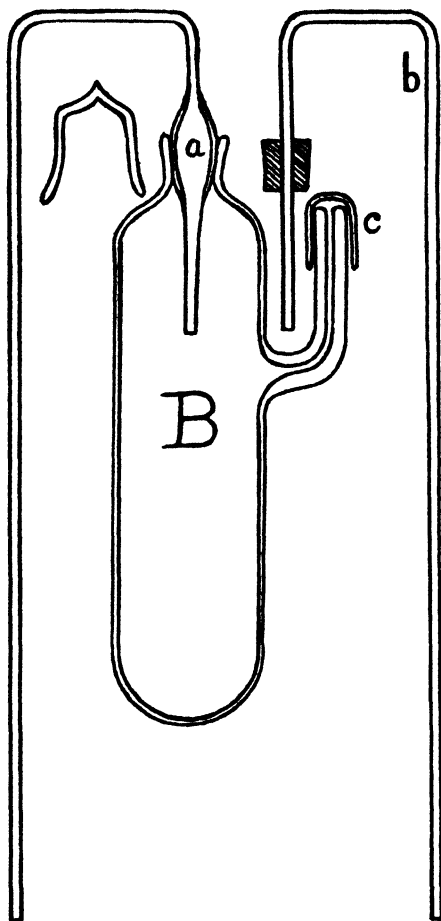
It was found advisable to rotate the tubes for at least four hours although in a few cases the saturation equilibrium was reached in a shorter period. In some experiments the agitation was continued for more than twenty hours but the results in these cases were essentially the same as in those where the solutions were analyzed after four hours' shaking. It was necessary to shake the solutions quite as long at the higher temperatures as at the lower.

After saturation had been attained, the tubes were allowed to stand in a perpendicular position in the thermostat for from two to four hours in order to allow all solid matter to settle. The dark color of the permanganate made it impossible to see whether the solution was absolutely free from small suspended particles of salt, and the nature of the permanganate made it inadvisable to attempt filtration of the solutions. However, since solutions after only two hours' standing showed the same salt content as similar solutions which had settled for four hours, it seems probable that no error was introduced from this source.

For removing the solution from the saturating tubes a pipette of the following form was used. A capillary tube with an enlargement at *a* was ground into the mouth of the bulb *B*. The pipette was filled by cutting off the top of the sealed saturating tube without removing it from the thermostat, inserting the capillary tube *a* into the saturated solution, and applying suction at *c*. *a* was then removed and both the mouth of the bulb *B* and the capillary side-tube were covered with glass caps. The bulb was wiped with a damp cloth, and, after it had been allowed to come to constancy in the balance case, was weighed. Evaporation from one of these pipettes was very slow. A solution at about 20°, on standing in a balance case containing sulphuric acid, lost only 3 mg. in fifteen hours. Since at higher temperatures the danger of evaporation is increased, the solutions were cooled with ice water as soon as they were removed from the saturating tubes.

With solutions saturated at the higher temperatures it was found necessary to warm the capillary tubes before pipetting out the solution, in order to avoid the deposition of crystals in the

enlargement *a*, although no salt deposited in the capillary itself. Capillary tubes of the form *b*, without an enlargement, were also used. These tubes were fitted into the bulb by means of a rubber stopper. The results with these tubes were no different from those obtained by warming the tubes of the form *a*.



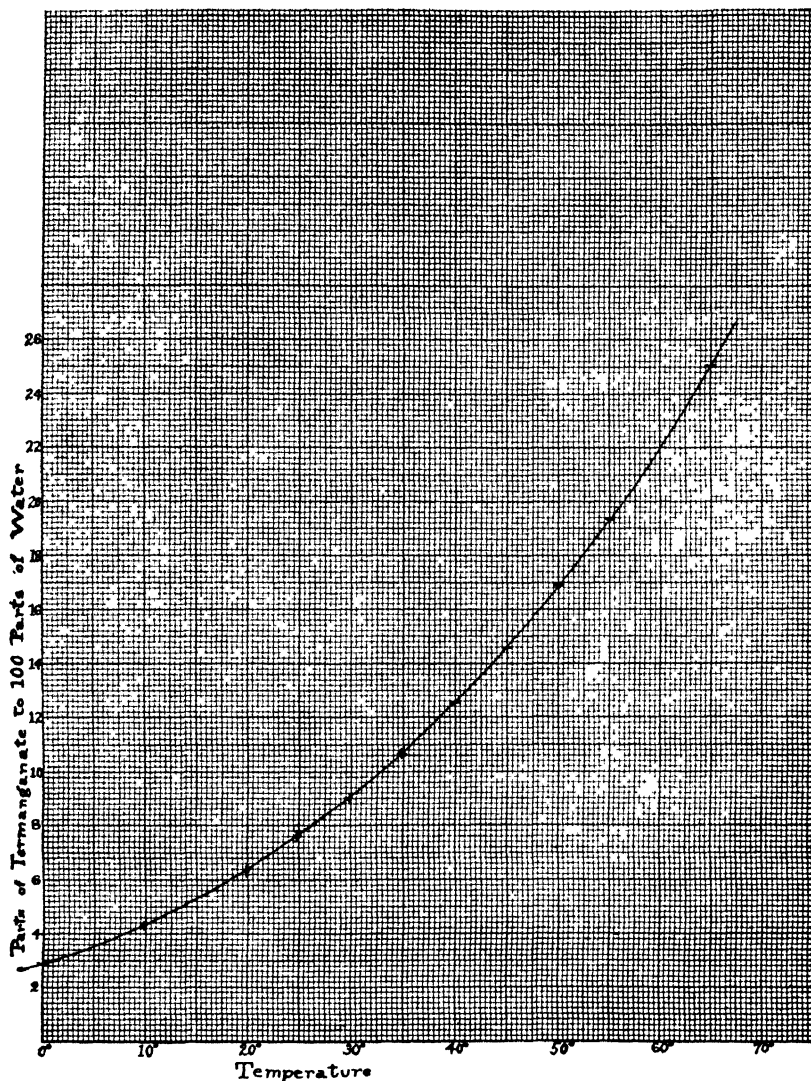
In order to make certain that saturation had been reached from below, the equilibrium was approached also from above. This was done by agitating the solution for an hour or two at a temperature from  $5^{\circ}$  to  $10^{\circ}$  above the temperature in question, and continuing the agitating at the desired temperature for from four to twenty hours. Experiments by this method gave pre-

cisely the same results as those where equilibrium was reached from the other direction.

Three methods of analyzing the saturated solutions were employed. The simplest and least satisfactory was that of evaporating weighed portions of the solutions to dryness in platinum crucibles and heating the residues to  $150^{\circ}$  in an air-bath. During the evaporation evidence of slight reduction of the permanganate always appeared. On the other hand it is improbable that all the water was expelled at  $150^{\circ}$ . A temperature much higher than this was found to produce considerable reduction of the salt. However, the two errors mentioned above would affect the results in opposite directions.

The second method of determining the permanganate was to weigh the potassium and manganous sulphates formed by reduction of the permanganate with sulphurous acid. The permanganate, after being weighed, was transferred to a platinum dish and was treated with a slight excess of sulphurous acid. The solution was then evaporated upon the steam-bath, first in the dish, then in a weighed platinum crucible. Finally the greater part of the excess of sulphuric acid was expelled upon a ring-burner and the last traces were eliminated by prolonged heating over a small Bunsen flame. Much care during the final heating was necessary to avoid partial decomposition of the manganous sulphate, with the formation of manganic oxide. It was possible, however, to obtain a product that gave a perfectly clear solution in water, showing that no decomposition had taken place, and which nevertheless was not acid to methyl orange. The sulphurous acid was made from concentrated sulphuric acid and copper, and was redistilled.

The third method of analysis was titration with oxalic acid. This acid was many times recrystallized, first from hydrochloric acid solution, then from water until free from chlorides. In order to bring it to the theoretical composition, it was finely powdered and exposed in a thin layer in a desiccator over sulphuric acid of the specific gravity 1.35. A slight deficiency of oxalic acid was weighed out and dissolved in water. Then, after the addition of a considerable excess of sulphuric acid, the permanganate was slowly introduced into the hot solution of oxalic and sulphuric acids. Finally the slight excess of permanganate was reduced by means of a fifth-normal oxalic acid solution. In a few cases



where the oxalic acid was in excess the end-point was reached by means of a standard solution of permanganate.

Since all three methods gave essentially identical results, it is highly probable that no constant errors affected any one of them to an appreciable extent.

In the following table the starred determinations were made with solutions which had been first supersaturated.

## 1341

Temperature.	Period of shaking. Hours.	Weight of solution Grams	Weight of $\text{KMnO}_4$ . Grams	Weight of $\text{K}_2\text{SO}_4$ 2 $\text{MnSO}_4$ . Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Grams.	Per cent. of $\text{KMnO}_4$ .
0°	4.5	12.489*		0.5190		2.759
	4.5	12.438			0.6838	2.758
	4.5	11.791		0.4902		2.760
	4.5	11.798			0.6461	2.747
	4.5	10.684*		0.4443		2.761
	4.5	9.686*			0.5297	2.743
	4.5	12.354*			0.6765	2.747
					Average,	2.754
9.8°	4	10.433*	0.4319			4.140
	4	8.924*			0.735	4.132
	4.5	10.098*	0.4176			4.136
	4.5	9.385*			0.772	4.127
	4	8.944*		0.5577		4.140
	4	9.340*			0.768	4.125
					Average,	4.133
19.8°	5	9.609	0.5737			5.970
	5	8.172			0.969	5.948
	18	10.624	0.6342			5.970
	18	10.624		0.9535		5.959
	18	9.012			1.066	5.934
	18	9.870		0.8879		5.973
	16	10.431*		0.9369		5.964
	16	8.870*			1.051	5.944
	16	10.480*			1.244	5.955
	16	9.051*	0.5394			5.960
					Average,	5.958
24.8°	4	11.368		1.2081		7.056
	4	11.018*		1.1716		7.060
	4	13.325*		1.4189		7.070
	5	11.301 <sup>1</sup>		1.2000		7.050
	5	14.793 <sup>1</sup>		1.5681		7.038
	5	13.686 <sup>1</sup>		1.4569		7.068
	28	15.758 <sup>1</sup>		1.6728		7.048
	23	12.191 <sup>1</sup>		1.2963		7.060
	5	14.932* <sup>1</sup>		1.5820		7.035
	5	13.939* <sup>1</sup>		1.4826		7.062
					Average,	7.055



Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $\text{KMnO}_4$ . Grams.	Weight of $\text{K}_2\text{SO}_4 \cdot 2\text{MnSO}_4$ . Grams.	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Grams.	Per cent of $\text{KMnO}_4$ .
29.8°	4	9.141		1.1391		8.274
	4	9.804		1.2237		8.287
	4	9.021			1.491	8.292
	3	9.015*	0.7474			8.291
	3	9.015*		1.1239		8.278
	3	9.972*		1.2440		8.283
	20	8.803		1.0963		8.269
	20	9.857			1.628	8.286
					Average,	8.283
34.8°	4	8.170*			1.5700	9.640
	4	8.691*		1.2652		9.666
	4.5	8.986			1.723	9.619
	4.5	11.202	1.0815			9.655
	4.5	9.874			1.892	9.613
	4	13.749			2.638	9.625
	4	9.694		1.4066		9.634
	4	8.542*			1.644	9.655
	4	6.675*		0.9715		9.664
	4	8.916*			1.717	9.661
					Average,	9.643
40°	18	10.934			2.4286	11.143
	18	9.498			2.1134	11.163
	18	9.374		1.5740		11.149
	18	11.123		1.8617		11.113
	18	10.704			2.3809	11.159
	18	11.245			2.4996	11.151
	18	11.774*	1.3174			11.189
	18	10.063*			2.2414	11.174
					Average,	11.155
45°	4	10.562*			2.682	12.739
	4	11.403*			2.895	12.736
	4	9.812			2.486	12.710
					Average,	12.728
50°	20	11.499			3.3095	14.438
	20	10.965			3.1571	14.443
	20	10.455		2.2764		14.457
	20	9.794			2.817	14.429
	36	12.182*			3.508	14.446
	30	11.896*		2.5920		14.465
					Average,	14.446

Temperature.	Period of shaking Hours	Weight of solution Grams	Weight of $\text{KMnO}_4$ Grams	Weight of $\text{K}_2\text{SO}_4$ 2 $\text{MnSO}_4$ Grams	Weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ Grams	Per cent of $\text{KMnO}_4$ .
55°	25	9 960			3 216	16.198
	25	9 995		2 4404		16 212
	25	8 675			2 802	16 203
	17	12 090*			3 904	16 199
	17	8 481*		2 0685		16 193
	17	8 675*			2 802	16 203
						<hr/> Average, 16 201
65°	4	7 801		2 3531		20 028
	4	6 987			2 744	19 988
	4	9 049			3 607	19 994
	4	7 810*		2 3597		20 060
	4	6 763*		2 0382		20 010
	4	6 809*		2 0555		20 043
						<hr/> Average, 20 021

Temperature Degrees	Per cent of $\text{KMnO}_4$	Parts of $\text{KMnO}_4$ to 100 parts of water
0	2 75	2 83
9 8	4 13	4 31
19 8	5 96	6 34
24 8	7 06	7 59
29 8	8 28	9 03
34 8	9 64	10 67
40 0	11 16	12 56
45 0	12 73	14 58
50 0	14 45	16 89
55 0	16 20	19 33
65 0	20 02	25 03

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## THE NITRIDES OF ZINC, ALUMINIUM AND IRON.

BY ALFRED H. WHITE AND L. KIRSCHBRAUN

Received July 19 1906

THE action of ammonia at high temperatures upon metals has already been investigated by Beilby and Henderson<sup>2</sup> who showed that almost all metals are profoundly modified in their physical properties upon exposure to ammonia gas at a red heat. In their experiments nitrides of approximately definite composition were formed from some metals, but in more cases the percentage of

<sup>1</sup> These determinations were prepared by Mr. Hubbard, the remainder by Mr. Boylston

<sup>2</sup> J. Chem. Soc. 79, 1245.

nitrogen fixed was small and variable, and frequently the only evidence that there had been combination between the nitrogen and metal was obtained from the porous structure after the operation.

We have studied the action of ammonia gas upon zinc, aluminium, and iron in as nearly a quantitative manner as possible and present here the results which are new. The apparatus and methods were in general the same as those previously employed by one of us in measuring the decomposition of ammonia at high temperatures.<sup>1</sup>

*Zinc Nitride and the Action of Ammonia upon Zinc.*—We have found no record in the literature of a previous study of this reaction. When ammonia was passed over granulated zinc at a temperature of 500° or below, no evidence of appreciable fixation of nitrogen could be detected on solution of the treated metal in acid. The most favorable temperature for the absorption of nitrogen seemed to be 600°, granulated zinc at this temperature taking up 2 per cent. of nitrogen in thirty minutes. The percentage absorbed was not increased by a longer stay in the furnace. Higher temperatures caused much volatilization of zinc without fixation of nitrogen. Sheet zinc at 600° gave only a trace of nitride. When ammonia was bubbled through molten zinc, fine particles were thrown up which stuck to the walls of the test-tube and contained as high as 3.7 per cent. of nitrogen. Zinc dust fixed a larger amount of nitrogen and the resulting product contained as much as 10.6 per cent. nitrogen, with a zinc content of 86.83 per cent. Although the temperatures employed were ordinarily 200° above the melting-point of zinc, zinc placed in a combustion tube heated to this temperature in a current of ammonia did not melt but retained the form of the material as it was placed in the tube. It became brown and dust-like on the surface and as the percentage of nitrogen increased became blacker. The nitride obtained from the zinc dust and which contained 10.6 per cent. of nitrogen was a powder, mostly black but mixed with a brown material. It was found possible to remove considerable of the brown powder by washing in alcohol, the brown powder staying in suspension and being poured off with the alcohol. The black powder remaining was washed with ether and dried *in vacuo* but it was noticed that the odor of ammonia was very

<sup>1</sup> This Journal, 27, 373.

noticeable when the desiccator was opened, and the percentage of nitrogen had not been increased by the washing process.

The decomposition of the ammonia in the synthesis of this nitride at  $600^{\circ}$  was only from 1.0 to 1.5 per cent. so that it did not seem that the hydrogen would have caused any very important reversal of the reaction. The stability of the nitride when heated in an atmosphere of nitrogen was tested at different temperatures. Samples heated to  $650^{\circ}$  and  $700^{\circ}$  for an hour did not change appreciably in appearance or in percentage of nitrogen. However, sublimed zinc in the cooler parts of the tube showed that there had been decomposition, but that it had proceeded no more rapidly than the sublimation of the zinc. The following series of experiments was then undertaken.

Duration of heating	Temp.	Loss of weight of nitride. Per cent
20 min.	$800-840^{\circ}$	60.1
1 hr.	$750$	63.0
1 hr.	$700$	26.0
1 hr.	$600$	6.3

These experiments show that the decomposition of zinc nitride begins below  $600^{\circ}$ , which is the temperature at which it may best be formed by the action of ammonia upon the metal, and that therefore it will not be possible to synthesize in this way a nitride of theoretical composition. The closest approach to it will be made by offering the greatest extent of metallic surface to the action of the ammonia, and thus accelerating the reaction. The higher absorption of nitrogen when the zinc was in the form of dust agrees with this view. The instability of the nitride at relatively low temperatures also indicates that it is useless to hope to bring about any considerable formation of nitride by direct union of the elements, although from the close relationship of zinc and magnesium in the periodic system, it had been hoped that zinc like magnesium could be made to combine directly with nitrogen.

Arons<sup>1</sup> has noted a slight combination of zinc and nitrogen between the poles of an electric arc maintained between zinc electrodes in an atmosphere of nitrogen, and Rossel<sup>2</sup> has observed a similar phenomenon when zinc and calcium carbide are heated in the air, but the only record which we have found of the preparation of a

<sup>1</sup> Chem. Centr. 11, 643 (1899).

<sup>2</sup> Compt. rend. 121, 941.

nitride of definite composition is that of Frankland,<sup>1</sup> who by heating zinc amide to 200° obtained a nitride to which he gave the formula  $Zn_3N_2$ . This theoretically contains 12.52 per cent. nitrogen. The highest percentage obtained in our experiments was 10.6 per cent., but in view of the facts just noted concerning the difficulty of preparing a nitride of theoretical composition by the action of ammonia upon metallic zinc, it seems probable that the nitride obtained in our experiments should be regarded as  $Zn_3N_2 + xZn$ . Whether this diluting zinc is to be regarded as a mechanical mixture or a solid solution is a point upon which we have no evidence except the fact that it was not possible by fractional solution to isolate either a definite nitride or to dissolve the nitride and leave a residue of zinc. Apparently, the nitride and its diluting zinc dissolved together which is, so far as it goes, an indication that the nitride is dissolved in the zinc as has been shown to be the case with nitride of chromium by Baur and Voerman.<sup>2</sup> The properties of our nitride of zinc agree with those given by Frankland.

*The Action of Ammonia upon Aluminium.*—The action of dry ammonia upon metallic aluminium was studied in the same way. The most favorable temperature for the absorption of nitrogen seemed to be higher than was the case with zinc and only relatively slight amounts of nitrogen were fixed. Only a trace of nitrogen was found in aluminium dust which had been heated for an hour and three-quarters at 600° in a stream of ammonia whose decomposition was only 0.4 per cent. At 750° in an hour and a quarter 1.54 per cent. of nitrogen was fixed, the decomposition of the ammonia being 1.0 per cent. The highest percentage of combined nitrogen was obtained at a temperature of 700°. After three hours the amount of nitrogen was 1.80 per cent. The nitride is decomposed by boiling water with evolution of ammonia. The fixation of nitrogen by aluminium was so small that it was not deemed practicable to determine its temperature of initial decomposition in an atmosphere of nitrogen.

*Nitride of Iron and Action of Ammonia upon Iron.*—The formation of nitride of iron through the action of ammonia upon metallic iron has received a great deal of attention in recent years. The very interesting experiments of Baur and Voerman before alluded

<sup>1</sup> Phil. Mag. [4] 15, 149.

<sup>2</sup> Z. physik. Chem. 52, 467.

to have shown that the dissociation pressure of the nitride at the lowest temperature at which ammonia will react with iron is many atmospheres, and that therefore it will never be possible in this way to attain a nitride of theoretical composition. It would be expected from analogy with the other bivalent elements, magnesium, barium, zinc and others, that the formula for the iron nitride would be  $\text{Fe}_3\text{N}_2$ . The usually accepted formula is  $\text{Fe}_2\text{N}$ , based entirely upon the analytical results, which show as the highest amount of combined nitrogen which has been obtained a trifle less than the 11.11 per cent. required for the compound  $\text{Fe}_2\text{N}$ . Our experiments have been no more successful than those of others in synthesizing a nitride with a higher percentage of nitrogen. The best results were obtained from iron reduced by hydrogen which, from its large surface, absorbed nitrogen rapidly.

This spongy iron begins to decompose ammonia below  $400^\circ$ , and at  $412^\circ$  in spite of a rapid stream of gas flowing through the apparatus, 1.0 per cent. of the ammonia was decomposed. That nitrogen was being absorbed was shown by the fact that the gas passing the acid of the nitrometer was 87.6 per cent. hydrogen instead of the 75 per cent. obtained when  $\text{NH}_3$  is decomposed by heat alone. The next gas analysis made when the furnace temperature was  $440^\circ$ , showed that the ammonia was decomposed to the amount of 3.4 per cent. and that the nitrogen was being almost quantitatively absorbed, the gas collected containing 96.2 per cent. hydrogen. The next test was made at a temperature of  $513^\circ$  and showed that nitrogen was being given off more rapidly than it was being absorbed, the gas in the nitrometer containing only 70.2 per cent. hydrogen. The proportion of ammonia decomposed was 12.8 per cent. The furnace was then allowed to cool with the ammonia passing through it. The nitride obtained contained 8.26 per cent. nitrogen. The most successful temperature was found to be  $450\text{--}475^\circ$ , but our best preparation yielded only 10.1 per cent. nitrogen, which is a few tenths of a per cent. less than some others have obtained. Varying percentages below this could be obtained according to the conditions.

Each of the preparations was analyzed by solution in dilute acid with measurement, and in many cases analysis of the gas evolved, titration of the dissolved iron, and distillation of the ammonia. The gases were always found to be pure hydrogen

and the sum of the iron and nitrogen to be above 99 per cent. If the hydrogen evolved during solution be calculated to free iron, and the difference between this figure and 100 per cent. called nitride, and the total amount of nitrogen be figured as being contained in this nitride, it will bring the percentage of nitrogen in the nitride to 14.5 per cent. as the average of determinations on nine samples, with a maximum of 15.1 and a minimum of 14.2. The percentage of nitrogen calculated on the total weight varied in these samples from 2.25 to 10.04, so that as far as analytical results show there is no break in the series, whose members may be regarded as either a mechanical mixture or a solid solution of iron and nitride of iron. The nitride of iron mentioned above corresponds closely to  $\text{Fe}_3\text{N}_2$  containing 14.35 per cent. nitrogen. The series might then probably be considered as  $\text{Fe}_3\text{N}_2 + x\text{Fe}$ , but so far as percentage calculations go, might equally well be considered  $\text{Fe}_2\text{N} + y\text{Fe}$ .

An analogy suggests itself between the nitride of iron and the carbide of iron. It is impossible to prepare the theoretical  $\text{Fe}_3\text{C}$  by direct union of carbon and iron. The resulting compound invariably carries a lower percentage of carbon. The theoretical carbide may however be isolated from any sample of slowly cooled iron which contains carbon, and we know that all such samples of slowly cooled steels are mechanical mixtures of iron and carbide of iron. This has been shown for steel in several ways but unfortunately the methods which have proven themselves most valuable in the investigations of the reactions of carbon and iron are inapplicable in the study of the nitrides, whose spontaneous decomposition prevents the study of cooling curves, and whose physical state as brittle fine wires or powder prevents the polishing necessary for a microscopic investigation. The impossibility of getting a solid bar of iron containing a high percentage of nitrogen prevents the application of the electrolytic method by which iron is dissolved away, leaving a pure carbide. An experiment was tried with a piece of sheet iron containing about 4.0 per cent. of nitrogen but no nitride could be isolated by electrolytic solution.

Solutions of the double chlorides of copper and potassium both neutral and slightly acid have proved useful in isolating some of the constituents of steel and their effect was tried on the nitrides. A qualitative test with nitrides containing 1.0 and 2.5 per cent. of

nitrogen showed them to be quickly attacked by a neutral solution. A sample with 6.2 per cent. nitrogen was slowly attacked while one with 8.0 per cent. of nitrogen was apparently unchanged even after two weeks. A quantitative experiment with a sample containing 8.2 per cent. nitrogen made from iron reduced in hydrogen was carried out by placing 0.100 gram of the nitride in a beaker with 10 cc. of neutral 30 per cent. potassium copper chloride. No copper was deposited nor was other sign of reaction visible, and after standing for six days at room temperature the residue was removed and analyzed. It had lost only 3 mg. in weight and contained 7.9 per cent. nitrogen as compared with the original 8.2 per cent. A parallel experiment made with a solution to which hydrochloric acid had been added until it was a decinormal solution, showed more marked action. After six days the powder had lost about 37 mg. in weight and its percentage of nitrogen was 7.05. Similar experiments with other nitrides confirmed these results. Nitrides with higher percentages of nitrogen were very slowly attacked, those with smaller percentages more quickly, but the concentration of nitrogen in the undissolved residue was practically unchanged. It seems almost impossible that this fine porous nitride could contain free mechanically mixed iron which would not be dissolved by neutral or slightly acid potassium copper chloride, reagents which will disintegrate and remove completely the iron even from white cast iron. The results far rather point to the conclusion that the material is practically homogeneous and that the nitrogen is probably present as a solution of nitride of iron in iron.

#### SUMMARY.

By the action of dry ammonia gas upon zinc dust at the most favorable temperature of  $600^{\circ}$  a nitride of zinc is formed. This has a marked dissociation pressure even at its temperature of formation and hence must always have a lower percentage of nitrogen than theory requires. Preparations were obtained with varying nitrogen content, the highest being 10.6 per cent. The formula  $\text{Zn}_3\text{N}_2$  requires 12.5 per cent. nitrogen. The properties of our nitride agree with those of the  $\text{Zn}_3\text{N}_2$  which Frankland obtained by heating zinc amide and it is to be regarded as a mixture, or solid solution, having the general formula  $\text{Zn}_3\text{N}_2 + x\text{Zn}$ .

When ammonia gas acts upon aluminium powder small amounts



of nitrogen up to 1.8 per cent. may be made to combine with the metal. The most favorable temperature is  $700^{\circ}$ .

The most favorable temperature for the formation of nitride of iron is  $450-475^{\circ}$ . On account of the high dissociation pressure of the nitride at this temperature the nitride formed must always contain less than the theoretical percentage of nitrogen. Preparations with 10 per cent. of nitrogen were scarcely appreciably attacked by neutral potassium copper chloride and although slowly attacked by acid solutions did not change their percentage composition. They can not therefore be mechanical mixtures of free iron and nitride and are preferably to be regarded as solid solutions, as is the case with nitride of chromium and chromium. From analogy with other bivalent elements iron should form the nitride  $\text{Fe}_3\text{N}_2$  and the preparations may be represented by the formula  $\text{Fe}_3\text{N}_2 + x\text{Fe}$ .

UNIVERSITY OF MICHIGAN,  
ANN ARBOR, July, 1906.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 100.]

## THE ELECTROLYTIC PRECIPITATION OF GOLD WITH THE USE OF A ROTATING ANODE.<sup>1</sup>

BY JAMES RENWICK WITHROW

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THE electrolytes used in this investigation were solutions of auric chloride in the presence of (1) potassium cyanide and (2) sodium sulphide. The rate of precipitation of the metal was especially studied. The results show that pure potassium cyanide is evidently a better electrolyte than sodium sulphide for this particular purpose.

The apparatus used in the experiments was similar to that described by Ingham.<sup>2</sup> The first series of experiments with the cyanide electrolyte was made under conditions prescribed by Exner.<sup>3</sup> They were as follows:

<sup>1</sup> From the author's thesis for the Ph.D. degree.

<sup>2</sup> This Journal, **26**, 1269.

<sup>3</sup> Ibid. **26**, 1256.

No	Gold taken Gram	KCN Grams	Dilution cc	Current Amperes	Volts	Time Minutes	Gold found. Grams
1 ...	0.1377	1 5	103	5	13 -10.5	10	0.1377
2. ..	0.1377	1.5	78	5	11 -10.5	10	0.1372
3 .	0.1377	1 5	78	5	10.5- 8.5	10	0.1372
4	0.1377	1 5	78	5	10.5-10	6	0.1378
5 .	0.1377	1 5	78	5	10.5- 9	4	0.1370

The deposits were washed without interrupting the current. Usually a liter of water was required for the purpose. They were of a beautiful gold-yellow color, and consisted of microscopic, very adherent needles. It was not found necessary to let them stand in a desiccator before weighing, but after the ether had been volatilized by the heat of the hand, the dish was rubbed with a chamois skin and placed on the balance pan where it came to a constant weight in a few minutes.

The results confirm Exner's observations in every particular. Even less time than mentioned by him is sufficient for complete precipitation.

To ascertain the minimum time in which it was possible to make a complete precipitation, the following trials were conducted :

No	Gold taken Gram	KCN Grams	Dilution cc	Current Amperes	Volts	Time Minutes	Gold found Gram
1	0.2754	2 5	80	5	8- 7	10	0.2747
2	0.2754	2 5	80	5		5	0.2706
3	0.2754	2 5	80	5	7 6- 6 7	6	0.2720
4	0.2754	2 5	80	5	7 5- 6 7	8	0.2754
5	0.2754	2 5	80	7	9 5- 9	7	0.2748
6	0.2754	2 5	80	10	14 5-13	2	0.2667
7	0.2754	2 5	80	10	17 -13	3	0.2724
8	0.2754	5 0	85	10	17 -10	3	0.2319
9	0.2754	2 5	80	10	16 -12	3	0.2704
10	0.2754	2 5	80	12	15	2	0.2476
11	0.2754	2 5	80	10	15	4	0.2750
12	0.2754	2 5	80	12	19 -12	3	0.2621
13	0.2754	2 0	55	12-10	21 -18	3	0.2742

An inspection of this table reveals the fact, as seen in Expts. 1 to 4, that eight minutes are necessary to precipitate all of the gold. On increasing the current to seven amperes the gold was completely deposited in seven minutes. In the eleventh trial fifteen amperes were used and only four minutes were consumed in the deposition. In the trials from the sixth to the eleventh foaming of the electrolyte led to loss.

To learn the result of a still greater concentration of the electrolyte, the following experiments were carried out:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
1....0.2621		1.5	150	0.27-0.2	3.9	none	130	0.2621
2....0.2621		2.5	80	8 -5	11 - 7.5	800	10	0.2621
3....0.2621		2.5	55	12	18 - 8.5	800	3	0.2588
4....0.2621		2.5	30	12	11 - 6.5	800	3	0.2611
5....0.2621		2.5	30	12	13	800	3	0.2618
6....0.2621		2.5	30	12	11.5- 6	800	3	0.2602
7....0.2621		2.5	30	12	11 - 9.5	800	3	0.2608
8....0.2621		2.5	55	12	18 -10	800	4	0.2620
9....0.2621		2.5	55	10	16 -11	800	4	0.2604
10....0.2621		5	60	12	17 -10	800	3.5	0.2585
11....0.2621		2.5	55	12	21	800	1	0.0959
12....0.2621		2.5	55	12	25	800	2	0.2406
13....0.2621		2.5	55	12	16 5-10.5	800	4	0.2619
14....0.2621		2.5	55	12	14 - 9	800	4	0.2614
15....0.2621		2.5	55	12	14 -12	..	4	0.2600
16....0.2621		2.5	55	12	11 -10	380	4	0.2494
17....0.2621		2.5	55	12	15 -10	600	4	0.2571
18....0.2621		2.5	55	12	19 -13	800	4	0.2615
19....0.2621		2.5	55	12	17 -12	800	1	0.1265
20....0.0621		2.5	55	12	18 -11	765	4	0.2612
21....0.2621		2.5	55	12	19 -12	900	4	0.2612
22....0.2621		2.5	55	13	21 -12	790	4	0.2606
23....0.2621		2.5	55	15	12.5-10	450	4	0.2546
24....0.2621		2.5	80	15	14 -13	450	4	0.2412
25....0.2621		2.5	75	15	16 -10	740	4	0.2610
26....0.2621		2.5	80	15	16 -10	850	4	0.2611

The conclusion drawn from this series was that a current of not more than ten amperes should be used, the other conditions remaining the same. Higher currents produced boiling of the electrolyte. There was also variation in the speed of the rotator, and these two factors militated against getting constant results in the minimum space of time. In the succeeding determinations, therefore, only the conditions found most satisfactory in the last series were employed:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found Gram.
1....0.2611		2.5	80	7.0	10	800	12	0.2611
2....0.2611		2.5	80	10.2-10	11.4-10	800	5	0.2612
3....0.2611		2.5	80	10	14.7-9.6	860	5	0.2598
4....0.2611		2.5	80	10	10 -8	620	5	0.2527
5....0.2611		2.5	80	10	14 -9.6	820	7	0.2614
6....0.2611		2.5	80	10.2-10	10.8- 9	...	7	0.2609
7....0.2611		2.5	80	10	14 -10	820	10	0.2612
8....0.2611		2.5	80	10	14 - 9	770	10	0.2616

No	Gold taken Gram	KCN Grams	Dilution cc	Current Amperes	Volts	Speed per minute	Time Minutes	Gold found Gram
9	0.2611	2.5	80	10	13 -9.5	800	7	0.2615
10	0.2611	2.5	80	10 -10.5	13.5-10	830	7	0.2611
11	0.2611	2.5	80	10	15 -12	795	1	0.1054
12	0.2611	2.5	80	10	13.5-9.5	850	2	0.2049
13	0.2611	2.5	80	10	13.5-9.5	815	3	0.2420
14	0.2611	2.5	80	10	15.5-10	820	4	0.2582
15	0.2611	2.5	80	10	14.7-9.6	860	5	0.2598
16	0.2611	2.5	80	10	14 - 9	810	6	0.2613
17	0.2611	2.5	80	10	14 -10.1	776	7	0.2614
18	0.2611	2.5	80	10	14 -10	830	7	0.2613

Beginning with Expt 5, the current of ten amperes was regularly employed with an accompanying speed in the rotator of 800 revolutions per minute. The electrolyte was not previously heated from without. The points in the curve marked "KCN No. 1" in the figure were obtained from the eleventh experiment. Upon substituting a more concentrated gold solution—one containing 0.5222 gram—the final series was obtained.

No	Gold taken Gram	KCN Grams	Dilution cc	Current Amperes	Volts	Speed per minute	Time minute	Gold found Gram
1	0.5222	5	60	10	10 -8	800	10	0.5216
2	0.5222	5	60	10 -10.2	10 -7.3	800	12	0.5226
3	0.5222	2.5	55	10 -10.8	14.5-9.6	800	10	0.5222
4	0.5222	2.5	55	10 -10.3	14 -9.4	810	12	0.5234
5	0.5465	3.5	60	10 -10.5	8.3-7	790	12	0.5461
6	0.5465	5	60	10 -10.2	9.3-8.3	790	1	0.1891
7	0.5465	5	60	10.2-10.5	8.3-7	800	3	0.4341
8	0.5465	5	60	10 -10.3	9.6-7.1	825	5	0.5286
9	0.5465	5	60	10	8.6-6.7	780	7	0.5437
10	0.5465	5	60	10.3-10	8.3-6.3	790	11	0.5468
11	0.5465	5	60	10	7.8-6.8	790	12	0.5467

From the first and second determinations it was seen that the gold was completely precipitated in ten to twelve minutes. No. 3 was then tried to see if less potassium cyanide could be used as it might exert a retarding influence on the rate of precipitation. The result was satisfactory but there was quite a perceptible deposit on the anode, resembling yellow pollen. This was probably an oxide of gold. It dissolved instantly in concentrated hydrochloric acid.

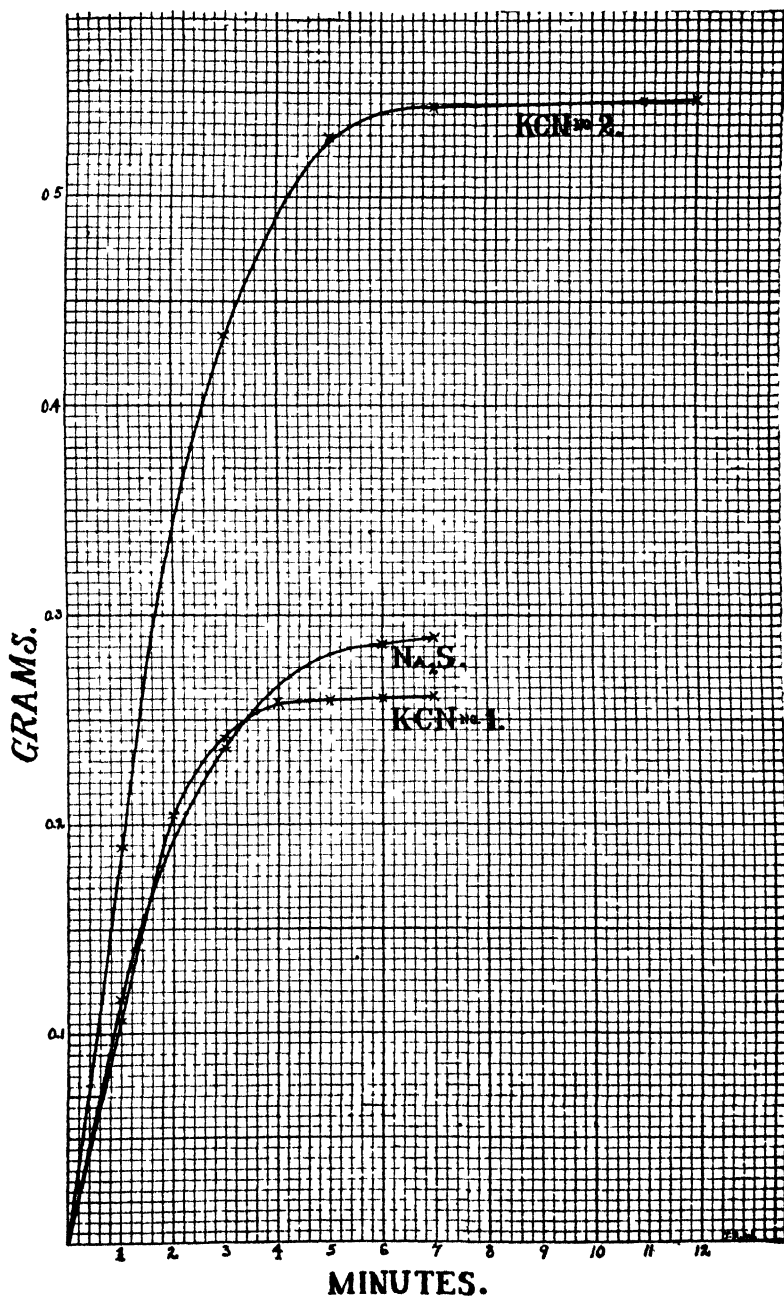
It may be mentioned here that this anodic stain or deposit was also noticed in several of the determinations, made with a station-

ary anode as checks on the work with the rotator. Especially was this so when the time of precipitation exceeded two hours. It was observed even with deposits weighing only 0.25 gram, with which amount it was never observed when the rotator was used, nor was it mentioned by Miller,<sup>1</sup> who, however, never precipitated more than 0.1697 gram of metal.

The anodic deposit having been eliminated by the use of an excess of potassium cyanide, the determinations from No. 6 on, furnished the points on the curve marked "KCN No. 2." Those deposits in which 0.5 gram of gold was completely precipitated were generally not so bright and were of a darker color than the 0.25 gram deposits.

Upon substituting sodium sulphide for potassium cyanide and electrolyzing the gold solution in its presence, very satisfactory results were obtained. The sodium sulphide was of the specific gravity 1.165. At the beginning, the gold solution was pipetted into a platinum dish and the sodium sulphide was added to it. This proved far from satisfactory because particles of gold sulphide adhered to the sides of the dish and it proved rather difficult to bring them completely into solution, so the expedient was adopted of first introducing the sodium sulphide solution into the dish, starting the rotator and then allowing the solution of gold chloride to run in from a pipette. No precipitate at all was formed and the liquid assumed a deep reddish brown or ferric sulphocyanide color, which, on heating, changed to a clear olive-green. The solution became cloudy during the decomposition from the separation of free sulphur. The anode was coated with a loose layer of sulphur. Rinsing with water sufficed to free the deposits from sulphur, after they were washed with hot water and dried in the usual way. The metallic deposits varied somewhat in color, that in Expt. 9 being beautifully burnished and rich yellow in hue. The curve marked  $\text{Na}_2\text{S}$  in the figure, was constructed from determinations made with 0.25 gram of metal in solution. It is worthy of note that the 0.25 gram curves in the two electrolytes—potassium cyanide and sodium sulphide—are almost identical. Probably they would have been exactly so if the same amounts had been used in each case.

<sup>1</sup> This Journal, 26, 1256.



No.	Gold taken. Gram.	Na <sub>2</sub> S. cc.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time Minutes.	Gold found. Gram.
1....	0.2878	15	60	10 - 8.8	7.6- 7.2	810	7	0.2891
2....	0.2878	30	60	10.1-10.3	6.9- 6	840	7	0.2879
3....	0.2878	30	60	9.8-10.1	7.8	830	7	0.2897
4....	0.2878	15	60	10 - 9.8	11.6-11.1	840	7	0.2898
5....	0.2878	20	60	10	11.6- 9	800	7	0.2905
6....	0.2878	30	60	10.2-10.5	8.8- 7.4	830	7	0.2883
7....	0.2878	20	60	10.1-10	9.1- 8.2	850	7	0.2885
8....	0.2878	15	60	10	11.5-10	840	7	0.2887
9....	0.2878	30	60	10.1-10	9.4-8.5	850	1	0.1165
10....	0.2878	30	60	10	8 - 7	850	6	0.2870
11....	0.2878	30	60	10 -10.2	9 -7.9	850	3	0.2365

It was also found that as much as 0.5 gram of metal could be completely precipitated in adherent form in a period of time not exceeding twelve minutes.

Another subject that received some attention was the electrolytic analysis of alkali halides. The complete determination of the components of such salts was shown by Smith to be quite possible when<sup>1</sup> using a mercury cathode and a silver-plated gauze as anode.

In an attempt to get iodine into an adherent deposit a rotator was used, thinking that the deposit might in this way be so compacted as to adhere firmly. The spiral cathode was accordingly rotated from 300 to 500 revolutions per minute, while a silver-plated dish was made the anode. The total dilution was about 70 cc. The following results were obtained:

No.	KI taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	Potassium		Iodine	
					found. Gram.	present Gram.	found Gram.	present. Gram.
1....	0.0400	..	2.5-2.4	15	0.0094	0.0094	0.0280	0.0306
2....	0.0400	....	2.8-2.7	16	0.0094	0.0094	0.0307	0.0306
3....	0.0400	....	3.0-2.8	18	0.0095	0.0094	0.0300	0.0306

The cover glasses and the inner sides of the dish were washed down with distilled water shortly before the end of the determination. When the deposition was complete the dish was washed either by the usual siphoning method without interrupting the current or it was immediately withdrawn and the contents poured into a beaker and then rinsed several times with small portions of distilled water and dried in an air-bath, as was done with the gauze in the previous work. The former method was the safer

<sup>1</sup> This Journal, 52, 890.

of the two and was the one generally employed. In either case the wash-waters were carefully preserved and titrated for the potassium hydroxide

Potassium chloride was tried in the same manner and very excellent, adherent deposits were quickly obtained.

No	KCl taken Gram	Current Ampere	Volts	Time Minutes	Potassium		Chlorine	
					found Gram	present Gram	found Gram	present. Gram
1..	0.0400	0.055-0.07	3.9-3.8	15	0.0207	0.0209	0.0190	0.0191
2..	0.0400	0.08	5	15	0.0208	0.0209	0.0206	0.0191
3..	0.0400	0.08 -0.08	3.8-3.4	10	0.0205	0.0209	0.0187	0.0191
4..	0.0400	0.08 -0.09	3.6	10	0.0205	0.0209	0.0192	0.0191
5..	0.0400	0.08 -0.09	4.2-3.8	10	0.0211	0.0209	0.0189	0.0191
6.	0.0400	0.08 -0.09	5 -4.7	10	0.0198	0.0209	0.0180	0.0191
7	0.0400	0.08 -0.09	6.3-4.7	10	0.0211	0.0209	0.0187	0.0191

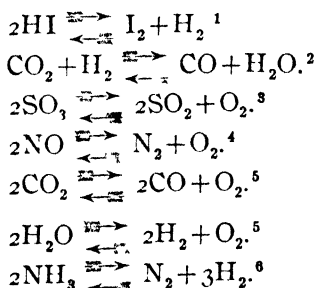
The same conditions were used as in the analysis of potassium iodide with aid of the rotator

UNIVERSITY OF PENNSYLVANIA

## THE DISSOCIATION OF WATER VAPOR AND CARBON DIOXIDE AT HIGH TEMPERATURES.

BY IRVING LANGMUIR

THE dissociation of gases at high temperatures has been the subject of many investigations during the past few years. In particular the states of equilibrium in the following reactions have been studied:



<sup>1</sup> Bodenstein: Z. physik. Chem. 29, 295 (1899).

<sup>2</sup> Hahn: Ibid. 44, 513 (1903); 48, 735 (1904).

<sup>3</sup> Knietzsch: Ber. 34, 4069 (1901); Bodenstein: Z. Electrochem. 11, 373 (1905).

<sup>4</sup> Nernst: Göttinger Nachr. 1904, Heft 4.

<sup>5</sup> Nernst and v. Wartenberg: Göttinger Nachr. 1905, Heft 1; Löwenstein: Z. physik. Chem. 54, 715.

<sup>6</sup> Haber and van Oordt: Z. anorg. Chem. 44, 341 (1905).



There are two general methods of determining the dissociation constants of gases at high temperatures. First, by the measurement, at the desired temperature, of some property of the gas which varies with the dissociation and which can be measured without disturbing the equilibrium. Such a property is the density. The second method is to heat the gas to the desired temperature and then by rapid cooling or by the removal of some catalytic agent to decrease the velocity of the reaction to a negligible quantity so suddenly that there is no time for a perceptible change to occur in the composition of the gas during the operation.

Each of the above-mentioned investigations except that of Löwenstein depended on the use of the second method. In all these experiments there is necessarily some change in the composition of the gases during the cooling. The important question, and one usually very difficult of solution, is whether this change is so small as to be negligible; the whole value of the results depends upon its being so.

It occurred to Prof. Nernst that around a glowing metallic wire, in a gas capable of dissociating, there would probably be only very slight recombination of the dissociation products, during the short time required for these to diffuse from the surface of the wires out into the comparatively cold layers only a short distance from the wire. Furthermore, if the wire had a sufficiently strong catalytic action there would be equilibrium at the surface of the wire and hence the cold gas some distance from the wire would have the same composition as it would have were the whole gas uniformly heated to the temperature of the wire.

At Prof. Nernst's instigation I undertook a series of experiments in the laboratory of Physical Chemistry of the University of Göttingen to investigate the dissociation of gases around glowing platinum wires in the hope of finding this prediction fulfilled and of so obtaining a new and convenient method for the determination of the dissociation constants of water vapor and carbon dioxide. Prof. Nernst suggested determining the temperatures by means of the change of electric resistance of the wire.

I wish here to express my appreciation of the interest taken in the work by Prof. Nernst and to thank him for many valuable suggestions.

Several investigators have carried out experiments to study the reactions in gases near and on the surface of glowing wires. For

example, recently, Haber and van Oordt<sup>1</sup> showed that traces of ammonia are produced when a mixture of hydrogen and nitrogen is passed over an iron wire heated to a bright red heat by an electric current. Emich<sup>2</sup> has shown that nitric oxide is slowly decomposed when brought in contact with white hot platinum wires. v. Hoffman<sup>3</sup> led steam with great velocity over white hot platinum wires and so obtained considerable quantities of hydrogen and oxygen.

All such experiments, however, have given only qualitative results. The reason that no quantitative determinations of the dissociation or association of gases by this method have been made is probably due partly to the difficulty of the determination of the temperature of the glowing wire and partly to the fact that no one foresaw that the degree of dissociation obtained by this method would really correspond to the equilibrium at the temperature of the wire.

Since I began these experiments Prof. Nernst, who has been endeavoring to get several independent ways of determining these very important constants, has published in conjunction with Dr. von Warterberg papers on the dissociation of water vapor and carbon dioxide. The experiments there described were carried out by passing the gases through porcelain tubes, shaped like pipettes, in an electric furnace. The difficulties to be overcome were so great that it seemed that the method of glowing wires would have many advantages.

Another method, also suggested by Nernst, was used in the investigation of Lowenstein who used "semipermeable membranes" of platinum to measure the partial pressure of hydrogen in water vapor heated in an electric furnace.

#### APPARATUS.

The apparatus used (see Fig. 1) for my experiments consisted of a difficultly fusible (Durax) glass tube of 0.9 cm. internal diameter, in the center of which a fine platinum wire was stretched. A little above the lower end was a bulb to give room for the electric connections. In order to measure the resistance of the wire accurately it was necessary to determine the ratio of "drop" to current between two points on the uniformly glowing wire.

<sup>1</sup> Loc. cit.

<sup>2</sup> *Monatsh.* 13, 78 (1893).

<sup>3</sup> *Ber.* 23, 2, 3314 (1890).

There were four platinum wires, A, B, C and D (0.3 mm. diameter) sealed into the glass. The wires A and B were used for supplying the current and C and D to measure the voltage between the two points P and P'. To avoid errors due to poor contacts one

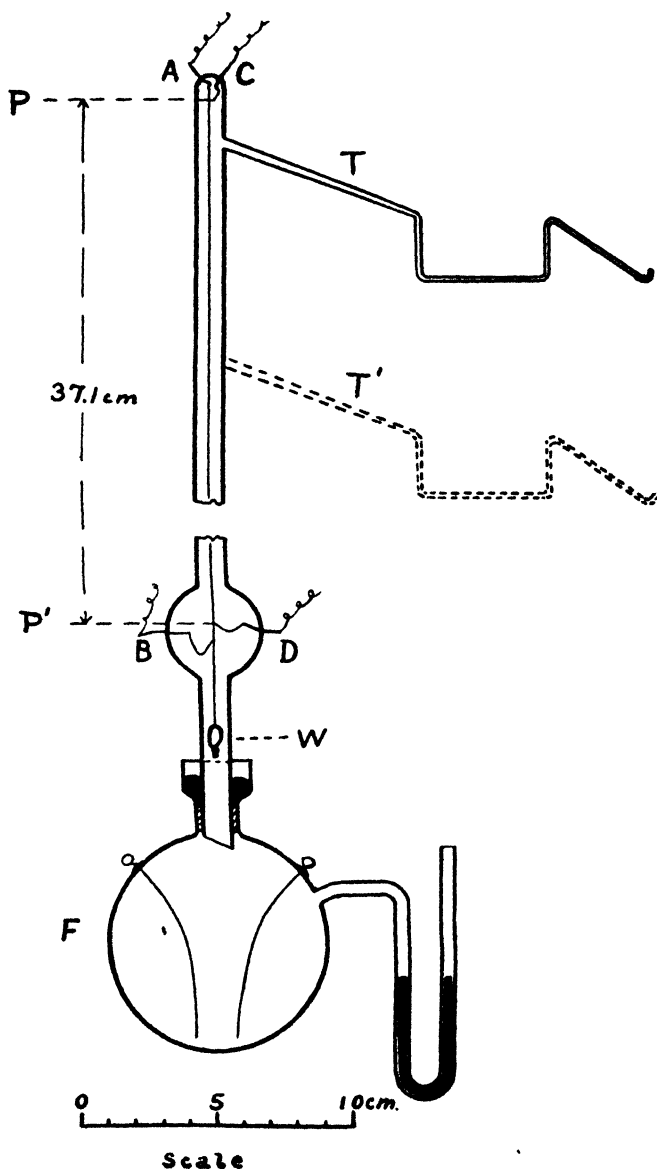


Fig. 1.

end of the main wire was fastened to C with silver solder and the other end similarly fastened to D. To A was soldered a short piece of wire, of the same kind as the main wire, and the other end of this was twisted around the main wire near its end so that the twisted part came between P and C. At P' a short piece of wire was twisted with the main wire so the twisted part was between P' and D. The other end of this piece had a small weight, W, of heavy platinum wire (about 2 grams) fastened to it to keep the main wire straight. A short distance below P' a piece of wire was twisted around the wire P'W with the twisted part down and the end of this short piece was soldered to B. All the twisted parts were carefully welded. The wire in the path of the current was thus made of the same diameter everywhere from A to B and glowed uniformly when heated by the current. The portion PA was made shorter than PC so that the tension of the wire insured good contact at P.

In the bulb the connections BP' and DP' were made sufficiently long to allow for the expansion (about 4 mm.) of the wire when heated. The connection BP' was made rather long, 1.5 cm., so that the gas upon entering the bulb would be rapidly heated to the temperature prevailing in the tube above, notwithstanding the cooling effect of the relatively large surface of the bulb.

When the wire was made to glow by an electric current, the temperature, to judge by the intensity of the emitted light, seemed to be perfectly uniform from A to B except within a distance of about 0.5 mm. from P and P'. But even at these joints themselves the wire would show a bright red heat when the rest of the wire was white hot.

The main wire was of the purest platinum that could be obtained from Heraeus. It had a diameter of 0.06 mm.

At the upper end of the tube a side tube, T, was attached. The internal diameter of this tube varied from about 2 mm. where it joined the main tube to about 0.6 mm. in the bent part. The object of bending it into the shape shown in the figure was to allow it to dip under the surface of the water in a beaker so that the water vapor passing through the apparatus would be condensed and could be collected over mercury together with any oxygen and hydrogen produced. The condensation occurred only after the first bend, that is, where the tube dipped under the water. The high velocity of the gases and the length of the

straight part of the tube prevented any hydrogen and oxygen diffusing back into the main tube.

The side tube T was joined to the main tube about 3 cm. below the end of the latter to avoid a possible change in the composition of the gases, due to the recombination of the dissociation products on the cooler platinum surfaces at the top of the tube. To be certain that this length of 3 cm. was sufficient to avoid error, one apparatus was made in which there were two side tubes, T and T', but it was found that the gases from each had the same composition.

In the experiments the apparatus was set up with the main tube vertical; the connections A and C were bent by means of a long glass rod so that the wire was exactly in the middle of the tube.

#### EXPERIMENTS WITH WATER VAPOR.

The steam was generated from a flask connected by a mercury seal directly below the main tube of the apparatus. In the flask were two electrodes of platinum wire to produce hydrogen and oxygen, if desired, along with the steam. In this way the equilibrium could be reached from both sides. The water in the flask contained a little sodium hydroxide to give it sufficient conductivity. The rate of boiling was regulated by a small flame, and the flask enclosed in an asbestos box. The heat given off by the wire prevented any condensation of the steam until it had passed under the water around the tube T. The water and the dissociation products were collected in a calibrated eudiometer which contained 3 cc. and which was subdivided to 0.02 cc.

The volume of gas and water was read off, then the gas exploded and a reading again taken. Then a little air was added and usually there was another explosion when sparks were passed. In this way the amount of hydrogen, oxygen and other gases could be determined. These results were corrected for temperature and pressure and solubility of the gases in water. As there was often a considerable excess of hydrogen it was necessary in some cases to consider the partial pressures of each gas in making the correction for solubility. As an example of this calculation let us take the data of one experiment (No. 67) and calculate the dissociation.

2.761 cc. water and 0.182 cc. gas were collected over mercury. The mercury and water column below the gas were equivalent to 2.8 cm. mercury. After the first explosion the gas volume was 0.096 over a column equivalent to 3.3 cm. mercury. Air was

now added until the volume was 0.420 (over 1.6 cm. mercury). Finally, after another explosion the volume was 0.318 (over 2.1 cm. mercury).

The barometer read 74.1 cm. and the temperature was 28°. The vapor-pressure of water at this temperature is 2.8 cm. mercury. The pressures of the dry gases for each of the four readings of volumes were 68.5, 68.0, 69.7 and 69.2 cm.

The volumes reduced to 0° and 76 cm. and the dry condition and calculated to the basis of 1 cc. of water are: Before first explosion, 0.054; after first explosion, 0.028; before second explosion, 0.125; after second explosion, 0.095.

Thus the decrease of volume ( $V_1$ ) on the first explosion was 0.026 and on the second ( $V_2$ ) 0.030.

The absorption coefficients in water are for  $O_2$ , 0.031;<sup>1</sup> for  $H_2$ , 0.018.

The pressure in the eudiometer was on the average 70 cm.; the volume of dissolved gases (at 0° 0.76 cm.) per cubic centimeter of water is then for  $H_2$

$$\frac{70}{76} \frac{\frac{2}{3}(V_1 + V_2)}{V_0} \times 0.018 = 0.011 \frac{V_1 + V_2}{V_0};$$

for  $O_2$

$$\frac{70}{76} \frac{\frac{1}{3} V_1}{V_0} \times 0.031 = 0.0095 \frac{V_1}{V_0}.$$

$V_0$  is the volume before the first explosion. In our example the dissolved gases amounted to 0.011 cc. of  $H_2$  and 0.0046 cc. of  $O_2$  per cubic centimeter of water.

Altogether then there was  $\frac{2}{3}(V_1 + V_2) + 0.011$  cc. hydrogen and  $\frac{1}{3}V_1 + 0.0046$  cc. oxygen or 0.040 cubic centimeter of oxygen and hydrogen in the proportion to form water and an excess of 0.022 cc. of hydrogen.

The excess of hydrogen was rarely as large as in the above example and was observed only in the first few experiments after filling the flask F with water, or in the experiments in which the water was electrolyzed. The excess of hydrogen is due to the presence of traces of ammonia in the water or to the separation of peroxide of lead at the anode by the electrolysis of lead salts formed by the action of the sodium hydroxide on the glass.

The volume of other gases (nitrogen from the air or from the decomposition of ammonia) is found to be

<sup>1</sup> Landolt-Börnstein's tables.

$$V_0 - V_1 - \frac{1}{2}V_2;$$

in our example 0.008 cc. per cubic centimeter of water.

The excess of hydrogen drives back the dissociation of the water vapor. We want in each case to know what the dissociation would be for equivalent amounts of hydrogen and oxygen. According to the law of mass action:

$$K = [H_2]^2 [O_2];$$

since the concentration of the steam may be considered constant, now  $[H_2]$  is proportional to  $\frac{1}{2}G + E$  where  $G$  is the amount of gas of equivalent proportions and  $E$  is the excess of hydrogen. Similarly,  $[O_2]$  is proportional to  $\frac{1}{2}G$ . If  $K'$  is a new constant, we have

$$K' = G(G + \frac{1}{2}E)^2 = G_0^3$$

where  $G_0$  is the amount of oxygen and hydrogen which would be found if there were no excess of hydrogen. Solving for  $G_0$  and expanding in a series we get

$$G_0 = G + E(1 - \frac{1}{2}E/G + \dots).$$

In most cases it is sufficiently accurate to write

$$G_0 = G + E.$$

If  $x$  is the degree of dissociation when there is no excess of hydrogen then,  $x = \frac{2}{3} \frac{G_0}{1246} = 0.000535 \times G_0$ . 1246 is the volume in cubic centimeters which 1 gram of steam would occupy at  $0^\circ$  and 76 cm. if the gas laws held down to  $0^\circ$ .

Returning to our example we have

$$\begin{aligned} G &= 0.040 & E &= 0.022 \\ \frac{1}{4} \frac{E^2}{G} &= 0.003 & G_0 &= 0.059 \end{aligned}$$

and  $100 x = 0.0032$ .

#### EXPERIMENTS WITH CARBON DIOXIDE.

In the experiments with carbon dioxide this gas was prepared from marble and 50 per cent. chemically pure nitric acid in a Kipp's apparatus. The marble was boiled several times in weakly acidulated water to free it from air and the acid was freed from air by a stream of carbon dioxide. The gas was purified by passing through a saturated sodium bicarbonate solution then through concentrated sulphuric acid and finally through a long tube containing phosphorus pentoxide. This tube had a bulb at one end with two platinum wires sealed in it between which sparks from a powerful induction coil were passed. In this way

8 per cent. of carbon monoxide could be produced and in these experiments, too, the equilibrium could be reached from both sides.

The carbon dioxide apparatus was connected to the dissociation apparatus by means of a mercury seal.

The gases passing out through the tube T were collected in 33 per cent. potassium hydroxide solution contained in an apparatus described by Nernst.<sup>1</sup> The mixture of carbon monoxide and oxygen were measured in a eudiometer which formed the upper part of the apparatus; the amount of carbon dioxide was found from the increase in the weight of the whole apparatus. Then the gas was exploded and the contraction noted. The only corrections needed were for temperature and pressure.

No excess of carbon monoxide could be detected in any case. In order to avoid solubility of the gases in the caustic potash, this was first shaken with a mixture of carbon monoxide and air. The eudiometer was calibrated and contained 5 cc.

After the carbon dioxide apparatus was freed from air the gas was very pure; only one part in 10,000 to 20,000 by volume was not absorbed in the caustic potash.

The degree of dissociation was calculated from the formula

$$x = \frac{2}{3} G \times \frac{1.96}{1000} = 0.00131 G.$$

G is the contraction on explosion (reduced to 0° and 76 cm.) per gram of carbon dioxide and 1.96 is the weight of a liter of this gas under standard conditions.

#### RESISTANCE OF THE WIRE.

In order to measure the temperature of the wire the resistance of the hot wire had to be measured and compared to the resistance at some lower temperature, 100° and room temperature being chosen. Thus the resistance had to be determined first with a current of 1 to 1.5 amperes flowing through it, and then with a current so small as to not perceptibly warm it. The Wheatstone bridge method could not well be used. The following method gave very satisfactory results and had the advantage that the resistance could be determined easily once every minute during the whole course of the experiment.

A constant resistance (N, Fig. 2) of 1.174 ohms was made of very thick constantan wire wound upon a large glass tube and the whole immersed in oil. A current of 1.5 amperes did not per-

<sup>1</sup> Nernst and v. Wartenberg: Göttingen Nach. 1905, Heft 1.



ceptibly warm this resistance. This known resistance and the wire in the dissociation apparatus were connected, by means of the wires A and B, in series, together with the variable resistance  $r$ .

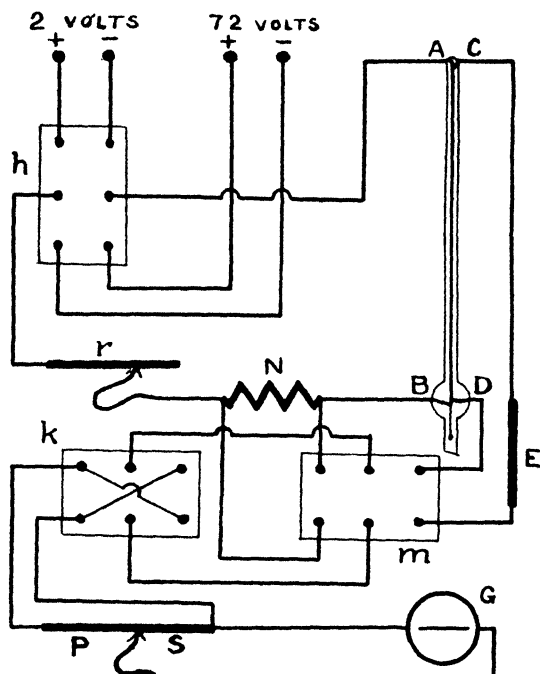


Fig. 2.

The two-way double switch  $h$  allowed either 2 or 72 volts to be used from a large storage battery, which gave a very constant current. The potential differences between C and D and between the two ends of N were then compared by means of the deflections obtained with a Deprez-d'Arsonval galvanometer, G. The resistances E, P and S were so chosen that the deflections were nearly equal for both potential measurements.  $k$  in the figure is a commutator and  $m$  a two-way double switch.

For measurements of the resistance at the various temperatures the following values of P S and E (in ohms) were used.

	P.	S.	E.
At room temperature.....	2000	500	20,000
At 100°.....	2400	500	30,000
At a red to white heat.....	2000	2	90,000

The resistance of the wire in the apparatus varied from 11 to

55 ohms, according to the temperature. The resistance of the galvanometer was 1077 ohms.

All resistances were carefully calibrated and the resistance of all connections measured and taken into account wherever these were not negligible. Although the system of wiring is rather complicated and a calculation of the resistance seems at first troublesome, it may be easily calculated from the formula

$$R = K - K \frac{\Delta e}{e_N}.$$

Here  $K$  is a constant to be determined once for all from the formulas

$$K = N \frac{E + P + S'}{P + S'}$$

$$S' = \frac{S}{1 + \frac{S}{G}}.$$

$e_N$  is the deflection of the galvanometer when connected with  $N$ .

$\Delta e$  is the difference between  $e_N$  and the deflection when connection is made with  $C$  and  $D$ .

The possible sources of error such as thermocurrents, elastic lag in the galvanometer, lack of proportionality between the deflection and the current in the galvanometer, imperfect insulation, etc., were considered and by commutation, reading the galvanometer at regular intervals, and by a careful arrangement of the wiring such errors were avoided or eliminated as far as possible.

With these precautions the resistances are probably always accurate to one part in 1,000 and usually to one part in 4,000.

The resistance at 100° was determined by boiling the water in the flask until all the air was driven out of the apparatus. The pressure of the steam was observed on the manometer on the side of the flask. A simple calculation shows that the conductivity of the water layer on the wire and on the walls of the tube can be entirely neglected.

#### STUDY OF THE ACCURACY OF THE METHOD.

Before proceeding with the determination of the temperature coefficient of the resistance, without which the temperature could not be accurately known, it seemed best to find out whether this

method for determining dissociations was capable of giving uniform and accurate results. For this purpose a series of about forty preliminary experiments were made.

Through an oversight of Heraeus a wire containing 10 per cent. rhodium was furnished in place of the pure platinum ordered, and only after the apparatus was constructed and several experiments had been made was it noticed that the temperature coefficient of the wire was much lower than that of platinum (only 44 per cent. as great). Since the temperature determination was not important for the preliminary experiments these were continued with the platinum-rhodium wire. The final series of experiments were made with platinum wire of exceptional purity as was proved by the high value of the temperature coefficient of the electric resistance (0.003909). This is a higher value than any that could be found in the literature except a practically identical value given by Holborn.<sup>1</sup>

Before each experiment the resistance of the wire at room temperature and at 100° was determined and then the resistance of the glowing wire measured several times in the course of the experiment.

The ratio of the resistances of the hot and cold wire served as a sort of temperature scale whose absolute value was not known. For the sake of convenience, however, let us speak of the temperature of the wire not as it is given in this scale, but as it was afterward found to be in the absolute scale, by comparison of experiments made with the two kinds of wires.

The results of the preliminary experiments and also a few facts about the usefulness of the method which were found from the experiments with pure platinum can be summarized as follows:

(1) The observed degree of dissociation  $x$  was the same whether the water was electrolyzed or not or whether sparks were passed through the carbon dioxide or not. This was true even when the temperature was as low as 1050° absolute and the current of gas as rapid as 0.6 gram  $H_2O$  or 0.3 gram  $CO_2$  per minute.

(2) Within wide limits  $x$  was independent of the velocity ( $S$ ) of the gas (in grams per minute).

In a series of experiments with steam the current was maintained constant and  $S$  was gradually increased from 0.09 to 0.6. The temperature of the wire and also  $x$  remained, however, en-

<sup>1</sup> Drude's Ann. 6, 242 (1901).

tirely unchanged. When  $S$  was increased still more, the temperature decreased somewhat because of the cooling effect of the cold gas;  $x$  also decreased. For example while  $S$  grew from 0.6 to 1.10 the average temperature of the wire fell  $20^\circ$  and  $x$  decreased 42 per cent. The temperature difference of  $20^\circ$ , however, corresponds to a decrease of  $x$  of 24 per cent.; that is, the error in  $x$  was 18 per cent. With this strong current of steam, one could easily see that the wire directly opposite the opening to the tube  $T$  (Fig. 1) glowed less brightly than the rest. The whole decrease of  $x$  was probably due to the recombination of the hydrogen and oxygen on this short (3 mm.) length of cooler wire.

From these experiments it appears that the equilibrium around the wire is reached with extraordinary rapidity. A value of  $S = 1.10$  corresponds to 33 cc. of steam at  $125^\circ$  per second or a linear velocity of 52 cm. per second. When one considers that the surface of the wire is only 0.7 sq. cm. it seems remarkable that 33 cc. can reach equilibrium in one second.

In another paper I will attempt to show theoretically that from this rapid rate of formation and by application of certain formulas which I have developed,<sup>1</sup> the observed value of  $x$  cannot differ from the value corresponding to the true equilibrium by more than  $10^{-12}$ ; that is, the observed dissociation must be identical with the equilibrium value.

(3) The resistance of the wire decreases about 2 per cent., while the temperature coefficient between  $20^\circ$  and  $100^\circ$  increases somewhat upon heating the wire for the first time. Upon further heating the wire changes very little if heated only in steam. In all the experiments the platinum-rhodium wire was heated altogether about twenty hours at temperatures between  $1200$  and  $1600^\circ$  (abs.). During the first five hours the resistance increased about 1 per cent., but in the remaining fifteen hours remained constant within the experimental error.

In the experiments with pure platinum wire the resistance increased slowly but steadily (about 1 per cent. in a long series of experiments). The wire had, however, become somewhat elongated. If one assumes the density of the platinum remained unchanged then the following relation should hold between the change of resistance  $\Delta R$  and the change of length  $\Delta L$ .

$$\frac{\Delta R}{R} = 2 \frac{\Delta L}{L}.$$

During eleven experiments a wire of 37.1 cm. length stretched 1.1 mm. The calculated increase of resistance is 0.60 per cent. Actually, the resistance at 20° increased 0.59 per cent. and at 100° 0.70 per cent.; that is, nearly within the experimental error.

Naturally, such lengthening of the wire introduces no error if the temperature coefficient remains unchanged.

In the preliminary experiments it was found that the value of  $x$  that was obtained depended solely upon the value of the ratio of the resistances of the hot and cold wire. The length of time the wire had been in use made no difference in this result.

Thus, eight preliminary experiments made at a temperature of 1440° (abs.) and distributed among all the preliminary experiments showed only irregular differences with a probable error of 2.9 per cent. in  $x$  for a single observation which corresponds to a temperature error of 3.0°.

The pure platinum wire, however, showed a tendency to give slightly increasing values for  $x$  as it was used even though the ratio of the resistances was kept constant. It seems then that the temperature coefficient of the resistance of platinum-rhodium remains constant but that of pure platinum decreases very slightly with continued heating.

(4) The lowest temperature at which the dissociation can be measured is about 1270° (abs.) as the gas formed then dissolves nearly completely in the water. Perhaps by determining the dissolved oxygen by chemical means it would be possible to work at much lower temperatures. The upper limit is set by the disintegration of the platinum, and it appears that a measurement of the dissociation is a very sensitive method of detecting disintegration ("Zerstaubung") of the platinum. When once the platinum-rhodium wire had been heated to 1650° (abs.) all further experiments gave too small values for  $x$ . For instance, after the wire was heated twenty-five minutes at 1670° (abs.) an experiment at 1460° (abs.) gave a value of  $x$  only 67 per cent. of what had previously been obtained at the same temperature. The explanation of this is that very finely divided platinum is deposited on the walls of the glass tube and that recombination of the gases occurs by catalysis. No deposit could be seen on the tube, but it was found that if the walls of the tube were rinsed out with aqua regia the original results could again be obtained.

With pure platinum wires no disintegration was observed either

in steam or in carbon dioxide up to temperatures of  $1550^{\circ}$  (abs.). Hulett and Berger<sup>1</sup> showed that in air disintegration occurs even at  $1073^{\circ}$  (abs.). It is therefore very important in these experiments never to heat the wire when air is in the apparatus. As was found later, heating in air also changes the temperature coefficient of the resistance.

By application of the law of mass action the effect of pressure on the degree of dissociation may be calculated. It was found that the variations of the barometric pressure from the normal had so small an effect on the dissociation that it could be safely neglected.

#### TEMPERATURE COEFFICIENT OF THE RESISTANCE.

According to Callendar<sup>2</sup> and Heycock and Neville<sup>3</sup> and particularly Harker,<sup>4</sup> one should be able to measure temperatures up to  $1000^{\circ}$  with great accuracy from the resistance if this is known for the three temperatures  $0^{\circ}$  and  $100^{\circ}$  and  $440^{\circ}$ . If  $R_t$  is the resistance at the temperature  $t$  then the following should hold

$$t - \theta = \delta \left\{ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right\}$$

where

$$\theta = \frac{R_t - R_0}{R_{100} - R_0} 100,$$

and  $\delta$  is a constant depending only on the purity of the platinum.

Holborn and Wien<sup>5</sup> measured the resistance of platinum wires up to  $1600^{\circ}$ . Unfortunately, the platinum they used was not very pure, since the temperature coefficient was only 90 per cent. of that which one gets from the wire that Heraeus now furnishes. Holborn and Wien found that above  $1000^{\circ}$  the resistance was a linear function of the temperature.

The resistance of the wire used in our dissociation experiments was determined at  $0^{\circ}$ , at  $100^{\circ}$ , and at the temperature of boiling sulphur. However, different values of  $\delta$  were obtained for different treatments of the wire. The wire was first heated to a red heat in air to anneal it. The following table shows the results of the tests on three wires.

<sup>1</sup> This Journal, **26**, 1512 (1904).

<sup>2</sup> Phil. Mag. **5**, 48, 519 (1899).

<sup>3</sup> Jour. Chem. Soc. Trans. **67**, 160 (1895).

<sup>4</sup> Proc. Royal Soc. **73**, 217 (1904).

<sup>5</sup> Wied. Ann. **56**, 360 (1895).

Wire No.	First heated to	During the time. Minutes.	$R_0$ .	$R_{100}/R_0$ .	$R_{444.6}/R_0$ .	$R_{1710}/R_0$ .	$\delta$ .
1.....	1640° (abs.)	15	1.0028	1.3909	2.6335	....	1.74
2.....	1640°	" 10	1.0202	1.3884	2.6338	6.20	1.57
3.....	1470°	" 16	1.0029	1.3902	2.6350	....	1.66
3.....	1470°	" 10	1.0022	1.3896	2.6387	.. .	1.56
3.....	1820°	" 4	1.0226	1.3880	2.6404	6 27	1.41

The resistances are accurate to 2 or 3 units in the fourth decimal place.  $R_{1710}$  is the resistance measured at the moment at which the wire melted when heated by a strong current. Since the temperature of the wire was not uniform (as the piece used was only 4 cm. long) the resistance measured must be considered only as a lower limit to the true resistance at 1710°, the melting-point of platinum.

The table shows that glowing the wire in air decreases the temperature coefficient between 0° and 100°, but increases it between 100° and 440°.

A comparatively large change in  $\delta$  corresponds to a small error in the temperature determination. Thus if  $\delta$  changes from 1.50 to 1.55 the calculated temperature at 1000° changes but 4°.

According to the table, when  $\delta$  is large  $R_{100}/R_0$  is also large and it thus happens that at high temperatures it makes very little difference which pair of values of  $\delta$  and  $R_{100}/R_0$  are chosen for the calculation of the temperature from  $R_T$ .

The final values chosen for a wire which had been in use a long time were

$$R_{100}/R_0 = 1.3900.$$

$$\delta = 1.55.$$

This method of determining the temperature of the wire by extrapolating from 440° is rather unsatisfactory and it was therefore used only as a control on the other method adopted. The results, however, may have an interest in themselves.

The final arrangement was to measure the resistance of the wire directly while it was being heated in an electric furnace. In order to avoid the errors due to the action of the air on the wire and to have conditions as nearly like those in the experiments as possible, a current of steam was passed through the furnace during the time of heating. The furnace consisted of a very thin-walled porcelain tube wound with platinum wire.

The wire which had been used in apparatus No. 5 was used for these measurements. After the last experiment (No. 86) had

been made the apparatus was broken and the wire removed, care being taken not to bend or stretch it.

The resistance of one piece of this wire was determined at  $0^{\circ}$ ,  $100^{\circ}$  and  $440^{\circ}$ . Another piece about 3 cm. long was wound around a small porcelain tube of 3 mm. diameter such as are used for thermo-elements. The turns were about 5 mm. apart. In this tube was brought the junction of a thermo-element near the middle of the coiled wire. To each end of the wire wound on the tube two platinum wires were welded; these, insulated in porcelain tubes, led out of the furnace. This bundle of porcelain tubes and wires was then placed in the electric furnace. The porcelain tube of the furnace was then connected with a brass tube for preheating the steam, a gas-tight joint being made by means of asbestos paper and water glass. After the furnace was heated to about  $200^{\circ}$  the superheated steam was passed in a gentle stream through the furnace. The resistance was then measured with the same apparatus that was used for all the other experiments. Two series of measurements were made. The thermo-couple was calibrated at the melting-point of antimony  $630.6^{\circ}$  and then, before and after each series of resistance determinations the reading of the thermo-couple was taken at the melting-point ( $1064^{\circ}$ ) of a short piece of pure gold wire placed about 3 mm. from the junction of the thermo-couple.

By moving the thermo-element back and forth in the tube it was found that the temperature over the whole length of the coiled wire was uniform.

The resistance at  $0^{\circ}$  (calculated from the resistance at room temperature and the temperature coefficient) was not just the same before and after the heating but it increased about 0.6 per cent. in each series. If this change is distributed over the observations at various temperatures the values for  $R_0$  are obtained that appear in the following table which gives the results of the experiments with the electric furnace.

V.	$R_0$ .	$R_T$	R.	T (abs.). Degrees.
7.513	1.638	6.495	3.965	1130
9.390	1.639	7.321	4.467	1298
10.63	1.642	7.816	4.760	1406
7.377	1.645	6.438	3.914	1117
9.391	1.646	7.390	4.490	1298
11.48	1.650	8.204	4.972	1477
9.33	1.654	7.375	4.459	1293



V is the voltage of the thermo-couple multiplied by 1000. The cold junction was at  $0^{\circ}$ . For the melting-point of gold V was found to be 9.83.

R is equal to  $R_T/R_0$ .

By plotting R and T one finds that up to  $T=1400$  the points lie in a smooth curve which does not differ very much from that obtained from the Heycock and Neville formula by using the values  $\delta=1.55$  and  $R_{100}=1.390$ . At  $T=1300^{\circ}$  the difference is about  $20^{\circ}$ .

If the curve be drawn through the points at  $T=1406^{\circ}$  and  $1477^{\circ}$  it appears that the curvature at about  $T=1350^{\circ}$  is greater than at lower temperatures, whereas from Holborn and Wien's paper it ought to be practically a straight line at this temperature. It seems probable that the cause of this is a slight conductivity at this high temperature of the porcelain on which the wire was wound and that therefore the results for R are slightly too low. The curve was drawn through the points at  $1200^{\circ}$  and carried to higher temperatures with approximately the same curvature that it has from  $1100^{\circ}$  to  $1300^{\circ}$ . The distance of the points at  $1400^{\circ}$  and  $1477^{\circ}$  from the curve then corresponds to  $8^{\circ}$  and  $10^{\circ}$  respectively. The curve was so nearly straight between  $1300^{\circ}$  and  $1550^{\circ}$  that it could be represented by the following formula without appreciable error.

$$T = 344.4 R - 247.$$

#### FINAL EXPERIMENTS WITH STEAM AND CARBON DIOXIDE.

With apparatus No. 4 a series of experiments were made to get the ratio of the dissociations of steam and carbon dioxide at different temperatures. Since this ratio varies very little with the temperature, it was not necessary to get the temperature accurately for these experiments. With apparatus No. 5 the object was to determine as accurately as possible the relation between the temperature and the degree of dissociation of water vapor, hence the wire of apparatus No. 5 was used for the determination of the temperature coefficient. The water was not electrolyzed and sparks were not passed through the carbon dioxide in these experiments for the preliminary work had shown such a treatment to be without material influence.

The results of these experiments are given in the following table. R is the ratio of the resistance of the hot wire to that at  $0^{\circ}$ . T is the absolute temperature. It was assumed that the

temperature coefficient of the wire in apparatus No 4 was the same as that in apparatus No 5

## EXPERIMENTS WITH APPARATUS NO 4

## Pure Platinum Wire

Experiment Number	S g gas per min	R	T (abs) Degrees	100 $\tau$	A	Average A	Remarks
30	0 14	5 00	1474	0 0140	3 746	3 7420	H <sub>2</sub> O
31	0 30	5 00	1474	0 0132	3 720		
33	0 25	5 15	1526	0 0225	3 753		
35	0 13	5 02	1481	0 0231	5 05	5 05	CO <sub>2</sub>
36	0 18	5 26	1565	0 0642	5 05		
37	0 43	5 00	1474	0 0135	3 730	3 728	H <sub>2</sub> O
38	0 48	5 00	1474	0 0134	3 727		
49	0 64	4 935	1451	0 0136	3 826	3 823	H <sub>2</sub> O
50	0 35	5 165	1531	0 0270	3 812		
51	0 45	4 94	1453	0 0139	3 829		
52	0 42	4 64	1351	0 0050	3 825		
53	0 12	4 77	1395	0 0140	5 168	5 161	CO <sub>2</sub>
55	0 18	4 77	1395	0 0144	5 176		
57	0 22	4 91	1443	0 0250	5 179		
58	0 20	5 07	1498	0 0471	5 201		
60	0 50	4 95	1457	0 0144	3 828	3 817	H <sub>2</sub> O
61	0 46	5 18	1537	0 0270	3 792		
62	0 47	4 96	1460	0 0150	3 831		

## EXPERIMENTS WITH WATER-VAPOR WITH APPARATUS NO 5

## Pure Platinum Wire

Experiment No	S g gas per min	R	l (abs)	100 $\tau$	A	Average A
67	0 30	4 559	1324	0 0032	3 755	3 753
68	0 27	4 670	1360	0 0045	3 733	
69	0 25	4 781	1399	0 0067	3 731	
70	0 26	4 870	1429	0 0100	3 780	
71	0 28	4 991	1471	0 0143	3 767	
77	0 32	5 007	1476	0 0150	3 769	3 778
78	0 43	5 232	1555	0 0292	3 762	
79	0 30	5 206	1545	0 0282	3 780	
80	0 33	5 000	1474	0 0149	3 761	
81	0 33	4 893	1437	0 0106	3 775	
82	0 35	4 770	1395	0 0072	3 783	
83	0 32	4 651	1354	0 0051	3 818	
84	0 31	4 564	1325	0 0033	3 765	
85	0 61	4 744	1386	0 0067	3 789	

Under A is a number obtained as follows: Nernst and v.

Wartenberg<sup>1</sup> give for the dissociation of steam at atmospheric pressure:

$$\log_{10} \frac{2(100x)^3}{(2+x)(1-x)^2} = [11.51] - \frac{25030}{T} + 2.65 \log_{10} \frac{T}{1000} - 0.00055(T-1000)$$

and for carbon dioxide

$$\log_{10} \frac{2(100x)^3}{(2+x)(1-x)^2} = [9.54] - \frac{29560}{T} + 2.97 \log_{10} \frac{T}{1000} - 0.00074(T-1000).$$

The numerical coefficients except those in brackets are all determined thermodynamically and do not depend in any way on the results of the experiments on the dissociation. Hence, for my experiments the same coefficients should apply if only new values are substituted for the quantities in the brackets. But it is more convenient to first simplify the expression. By neglecting  $x$  compared to 1 and by division by 3 we obtain for steam

$$\log_{10} x = A_{\text{H}_2\text{O}} - \frac{8343}{T} + 0.88 \log_{10} \frac{T}{1000} - 0.00018(T-1000) \quad (1)$$

for carbon dioxide

$$\log_{10} x = A_{\text{CO}_2} - \frac{9853}{T} + 0.99 \log_{10} \frac{T}{1000} - 0.00025(T-1000) \quad (2)$$

$A_{\text{H}_2\text{O}}$  and  $A_{\text{CO}_2}$  are then to be found from the experiments; the same values should be obtained no matter at what temperature the experiments were made. From Nernst's experiments the values are

$$A_{\text{H}_2\text{O}} = 3.83.$$

$$A_{\text{CO}_2} = 5.18.$$

A change in  $A$  of 0.01 corresponds to a change in  $x$  of 2.3 per cent. A small error  $\Delta T$  in the temperature measurement makes a corresponding error in the value of  $A$  ( $\Delta A$ ) which for temperatures not too far from  $T = 1400^\circ$  is given by

for steam

$$\Delta T = -109 \left( \frac{T}{1000} \right)^2 \Delta A, \quad (3)$$

for carbon dioxide

$$\Delta T = -93 \left( \frac{T}{1000} \right)^2 \Delta A. \quad (4)$$

<sup>1</sup> Göttingen Nachrichten.

## DISCUSSION OF THE RESULTS.

The values of  $A$  in general seem to be independent of the temperature and the velocity of the gas current  $S$ . Experiments in which the temperature is below  $1400^\circ$  (abs.) often give values of  $A$  which differ considerably from the mean, but these differences are so irregular that they are probably due simply to the relatively inaccurate determination of the very small quantities of gas appearing at these low temperatures.

The longer the wire has been in use, the larger the values of  $A$  become. As was mentioned before this change does not occur to an appreciable extent with platinum-rhodium wire. During the determination of the temperature coefficient the same change was undoubtedly going on. The value of  $A$  which corresponds to the temperature measurements is then somewhat larger than in Expts. 77-85. As the most probable value we may take

$$A_{\text{H}_2\text{O}} = 3.79.$$

From Expts. 30-38 we get

$$A_{\text{H}_2\text{O}} = 3.734 \quad A_{\text{CO}_2} = 5.050,$$

and from Expts. 49-62

$$A_{\text{H}_2\text{O}} = 3.820 \quad A_{\text{CO}_2} = 5.181.$$

The deviation of  $A_{\text{H}_2\text{O}}$  from the value 3.79 can only be caused by errors in the temperature measurement ( $\Delta T$ ). This error must naturally be the same for the experiments with carbon dioxide as for those with steam. Thus in equation (3) and (4) the values of  $\Delta T$  are equal and we have

$$\frac{\Delta A_{\text{CO}_2}}{\Delta A_{\text{H}_2\text{O}}} = \frac{109}{93}.$$

For Expts. 30-38

$$\Delta A_{\text{H}_2\text{O}} \text{ is } 0.056;$$

therefore

$$\Delta A_{\text{CO}_2} = 0.066;$$

hence

$$A_{\text{CO}_2} = 5.116.$$

Similarly, Expts. 49-62 give

$$A_{\text{CO}_2} = 5.147.$$

Expts. 47-64 were much more carefully made than Expts. 30-38, and since too low results can occur much more easily than too high results the most probable value seems

$$A_{\text{CO}_2} = 5.15.$$

From these results for  $A_{H_2O}$  and  $A_{CO_2}$  with the help of (1) and (2) we can calculate the dissociation at all temperatures at atmospheric pressure. At exceedingly high temperatures one must substitute

$$\sqrt[3]{\left(1 + \frac{x}{2}\right)(1-x)^2} \text{ in place of } x.$$

The following table gives the dissociations as calculated for various temperatures.

T (abs.).	100 $x$ for $H_2O$	100 $x$ for $CO_2$ .
1000	0.000028	0.000020
1200	0.000745	0.00093
1300	0.00266	0.00407
1400	0.00787	0.0146
1500	0.0197	0.0436
1600	0.0446	0.110
1700	0.0920	0.260
1800	0.170	0.546
1900	0.302	1.04
2000	0.504	1.84
2200	1.21	5.00
2500	3.38	15.6
3000	11.1	48.5

These values for the dissociation are 9.5 per cent, in the case of steam, and 7 per cent., in the case of carbon dioxide, lower than those of Nernst. These differences however correspond to temperature differences of only  $8^\circ$  and  $6^\circ$  respectively.

The possible sources of error in this method lie almost entirely in the measurement of the temperature. It seems probable that the error in the temperature determination is not over  $5^\circ$  and almost certainly not over  $10^\circ$ .

#### SUMMARY AND CONCLUSIONS.

First. It is shown that when water vapor or carbon dioxide is passed through a tube containing a glowing platinum wire, amounts of dissociation products are obtained which correspond to the dissociation equilibrium at the temperature of the wire.

Second. The degree of dissociation of water vapor and carbon dioxide were determined by this method and results were obtained which for water vapor were 9.5 and for carbon dioxide 7 per cent. lower than those previously obtained by Nernst by another method.

Third. In determining the temperature of the wire the temperature-coefficient of the electric resistance of pure platinum up to  $1200^{\circ}$  was measured.

Fourth. It was found that platinum and platinum-rhodium wires do not disintegrate perceptibly in steam or in carbon dioxide up to  $1300^{\circ}$ . At  $1400^{\circ}$  platinum-rhodium begins to disintegrate in steam.

The method of determining the dissociation of water vapor and carbon dioxide by means of glowing wires has many advantages. The apparatus is simple and the experiments are quickly made.

The great rapidity of cooling of the gases insures accurate results for every reaction where the substance of the wire has a strong catalytic action.

The only serious difficulty lies in the determination of the temperature of the wire. A modification of the method by which instead of a wire a platinum tube or other surface of platinum is used might be very useful in some cases. The outer surface of the tube should be exposed to the dissociating gas. The temperature could then be determined either by a thermo-element inside the tube or by optical methods.

For the determination of the dissociation under high pressures the method would present great advantages. It would be a difficult task to make a tube which could withstand very high pressure at  $1300^{\circ}$  or  $1400^{\circ}$ , but to heat a wire to that temperature in a tube containing gas at a very high pressure is a comparatively easy matter. Such an arrangement would be well adapted for the study of the formation of ammonia from the elements since not only the velocity of the reaction, but also the amount of ammonia corresponding to the equilibrium would be much increased by high pressure. A few rough experiments have been made with ammonia and it seems the method would be capable of giving good results.

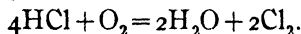
Another case in which this method may be of use is in determining the temperature of platinum wires or other platinum bodies. As v. Wartenberg has shown, temperatures may be accurately determined by means of the dissociation of steam. If the object is platinum, it need only be surrounded by steam and some of the steam withdrawn and analyzed in order to determine the temperature accurately.

## EQUILIBRIUM IN THE DEACON PROCESS.

BY GILBERT NEWTON LEWIS.

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IN THE well-known process for making chlorine, invented by Deacon, a mixture of air and hydrochloric acid gas is led over a rough surface impregnated with cupric chloride, kept at a temperature of about 400°. The cupric chloride acts only as catalyzer and may be replaced by the chloride of iron, nickel or cerium. The reaction is simply,



This reaction never runs completely to an end, but approaches a state of equilibrium which, according to the conditions of temperature and concentration, fixes a definite limit to the yield of chlorine which it is possible to attain.

Reliable data concerning this equilibrium have not been obtained hitherto. A number of investigations have been made to determine the yield of chlorine in the Deacon process under actual working conditions, in which ordinarily the gases are sent past the catalyzer too rapidly for the establishment of equilibrium. The most extensive research of this kind is one by Lunge and Marmier.<sup>1</sup> It seems not unlikely that at the highest temperatures at which they worked equilibrium was frequently reached. We shall return later to a consideration of their results.

The present investigation of this equilibrium was undertaken partly on account of the technical significance of the process, but more especially because a knowledge of this equilibrium enables us to find at any temperature the difference between the free energy of formation of hydrochloric acid and that of water, two data of fundamental importance in chemistry. In particular, this study will permit a new calculation of the potential of the oxygen electrode, for which I have recently found a value differing by more than one-tenth of a volt from the one commonly accepted.<sup>2</sup>

### EXPERIMENTAL METHOD.

The thermostat used in the following experiments was a modification of one that I have previously described.<sup>3</sup> It consisted

<sup>1</sup> *Z. angew. Chem.* 1897, p. 105.

<sup>2</sup> *This Journal*, 28, 158 (1906); *Z. physik. Chem.* 55, 465 (1906).

<sup>3</sup> *P. Am. Acad.* 40, 719 (1905); *Z. physik. Chem.* 52, 310 (1905).

in a fused mixture of sodium and potassium nitrates, in nearly equal proportions, contained in a vessel of enameled iron.<sup>1</sup> This vessel was surrounded by asbestos cloth upon which an electric heating coil of nickel steel wire was wound. The whole was packed in loose asbestos in order to avoid too great loss of heat. A current passed continuously through this outer coil, sufficient to heat the thermostat nearly to the desired temperature. The remainder of the heating was done by another electric heater<sup>2</sup> which was directly immersed in the bath and connected with the thermal regulator.

This regulator consisted of a hollow steel cylinder, holding about 300 cc., from which a steel tube of small bore led out of the thermostat to a height of nearly two meters; at the upper end it was joined to a glass capillary. The whole was filled with mercury, which on expanding made contact with a platinum wire in the glass capillary and thus operated a relay which broke the current in the inner heating coil. On account of the height of the mercury column, the thermostat could be used at temperatures far above the boiling-point of mercury.

The thermostat was well stirred and gave entire satisfaction. Without any readjustment it would run night and day for weeks without changing in temperature as much as a degree.

The temperatures were measured with a mercury thermometer. In order to eliminate the correction for the exposed stem, the thermometer was surrounded by a glass tube, about 4 cm. in diameter, in which the liquid of the bath could be drawn up nearly to the top of the mercury column. The liquid was thus raised and lowered several times until the thermometer gave a constant reading. Under the same conditions the thermometer was standardized by comparison with an accurately calibrated thermocouple which was kindly placed at my disposal by Mr. R. D. Mailey.

The apparatus in which the experiments were carried on is sketched in Fig. 1. Inside the thermostat (dotted lines) was situated the chamber *E* in which the reaction occurred. It was a

<sup>1</sup> The ware known as agateware is the only one which I have found satisfactory for this purpose.

<sup>2</sup> This heater was made by the Simplex Electric Co., of Cambridge, Mass., and proved very serviceable. It was simply a resistance wire, wound with asbestos, and enclosed in a spiral tube of copper.



glass cylinder of about 200 cc. capacity, half filled with the catalyzer and then drawn out at both ends and sealed to stout capillaries, which led out of the thermostat. One of these tubes, *D*, connected with the reservoir *B*, which contained the mixture of oxygen and hydrochloric acid. This reservoir was a 10-liter bottle joined by a siphon to a similar bottle, *A*. The gaseous mixture was kept over strong sulphuric acid.

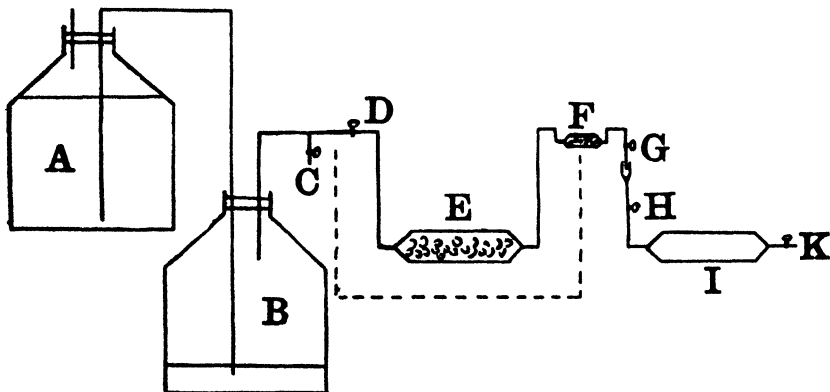


Fig 1.

The hydrochloric acid was made from strong sulphuric acid and a solution of chemically pure hydrochloric acid. The oxygen was prepared by heating potassium permanganate. In the desired amounts these gases were introduced into *B* through *C*, forcing the sulphuric acid through the siphon into *A*, whence it later flowed back into *B* as the gas was drawn off. The hydrochloric acid dissolved somewhat in the strong sulphuric acid, and diffused through it, thus causing a slight change in the composition of the mixture from day to day.

The gas was introduced into the catalyzing chamber through *D* and after remaining there a suitable time was withdrawn for analysis through *F G*. As the gases were being removed the water vapor which was produced during the reaction showed a tendency to deposit on the colder part of the exit tube. Water thus condensed would dissolve considerable quantities of hydrochloric acid and thus vitiate the analysis. To avoid this difficulty, the tube *F*, containing glass beads saturated with strong sulphuric acid, was inserted in the exit tube. It was placed outside the thermostat, but near enough to be kept warm by it. The sulphuric acid soon became saturated with oxygen, chlorine and

hydrochloric acid, after which it allowed these gases to pass through in unchanged proportions, removing only the water vapor.

The bulb *HI* was so made that its end fitted over the end of the exit tube and could be made tight by a rubber connection. The gases from *E* were drawn into this bulb, after which it was removed and the gases analyzed, as will be described below.

The catalyzer was pumice stone, broken into pieces about the size of a pea, cleaned by boiling with hydrochloric acid, and then saturated with a 10 per cent. solution of cupric chloride. It was then dried in a current of dry hydrochloric acid gas at 250°, until it ceased to give off water. This frequently took several days. The last part of the drying was done inside the catalyzing chamber.

That part of the glass apparatus which came in contact with the fused nitrates of the bath proved very fragile and the work was much delayed by breakages. For very generous aid in the construction of several of the catalyzing cylinders I wish to express my thanks to Mr. C. A. Kraus.

The method of carrying out the experiments was as follows: The tube *I* was exhausted, stop-cocks *K* and *H* being open, *G* and *D* closed. *K* was then closed, and *G* opened for an instant, during which a certain amount of gas passed from *E* into *I*. After *G* was closed *D* was opened, allowing the gas from *B* to pass into *E*, where it was left for half an hour or more. The process was then repeated over and over in order to establish constant conditions in the catalyzing chamber and the drying tube *F*. When finally these constant conditions were reached the tube *I* was removed after each filling (stop-cocks *G* *H* and *K* being closed) and the contents analyzed for oxygen, chlorine and hydrochloric acid, in the manner described below.

Each time when the gas had been left in the catalyzing chamber for the desired time, and just before the tube *I* was attached for drawing off the gas, a manometer was joined to the end of the exit tube and the stop-cock *G* turned for an instant. This gave the pressure in *E*. A rough measurement sufficed, for a change in pressure affects the equilibrium but little.

The analysis of the mixture in *I* was made in the following way: The stop-cock *K* was opened under a solution of pure potassium iodide, about one-fifth normal, prepared from water freshly boiled and cooled. The bulb was then shaken until all the chlorine

and hydrochloric acid were dissolved. The gas remaining was nearly pure oxygen. It was measured in a gas burette, and then absorbed in pyrogallol in order to determine the amount of impurity.

The iodide solution was titrated with thiosulphate, about one-tenth normal, and when the iodine, which had been set free by the chlorine, was just neutralized, phenolphthalein was added and the same solution titrated with one-twentieth normal alkali (potassium hydroxide, with a little barium hydroxide). This method of successive titration with thiosulphate and alkali has been used by Lind.<sup>1</sup>

In this way the oxygen, chlorine and hydrochloric acid could all be separately determined. However, in all the later experiments, since it was found that the amount of oxygen present could be calculated with sufficient accuracy from the composition of the original mixture, only the ratio of chlorine to hydrochloric acid in the final mixture was determined. The procedure was then much simplified. It was no longer necessary to take pains to produce a thorough vacuum in the tube *I* before the gas was let in. Furthermore, it was no longer necessary to use a large volume of iodide solution and the titrations could therefore be made with greater precision.

The composition of the original mixture was determined as follows: The bulb *I* was attached to *C* and filled with gas from the reservoir at a pressure slightly above that of the atmosphere. One of the stop-cocks was then opened for a moment and the gas allowed to come to atmospheric pressure. Water was then allowed to run in until the hydrochloric acid was completely absorbed and the pressure was again that of the atmosphere.

During the whole process the bulb was kept at a known constant temperature. It was then weighed. From this weight, together with the weights of the bulb empty and full of water, the proportion of hydrochloric acid and oxygen could be readily determined, allowance being made for the pressure of aqueous vapor. In order to make sure that the gas left in the bulb was pure oxygen it was absorbed in pyrogallol. The volume of the residue never amounted to more than a small fraction of a per cent. of that of the original mixture and was corrected for.

<sup>1</sup> Dissert. Leipzig, 1905.

## EXPERIMENTAL RESULTS.

For some time no concordant results could be obtained. This proved to be due to slow changes in the catalyzer. The method adopted does not permit the direct determination of the amount of water produced in the reaction. We assume that it is equivalent to the quantity of chlorine produced, but if the catalyzer gives up either water or chlorine this will not be true. It was found necessary, therefore, to pass a mixture of given composition over the catalyzer until the latter reached such a condition that it suffered no further change. At  $352^{\circ}$ , the lowest temperature at which experiments were made, several days were required, and frequently a week, before this stationary condition was reached.

Just what the change in the catalyzer is I am unable to say, but the experiments showed that in the presence of a mixture containing a large excess of oxygen, considerable quantities of oxygen were taken up by the catalyzer. If later a mixture with an excess of hydrochloric acid was passed through, the oxygen was set free once more in the form of water. Probably in the first case the oxygen set free chlorine, forming an oxide or oxychloride of copper. In the second case this oxide or oxychloride united with the hydrochloric acid to form normal chloride again and water.

If the oxide (or oxychloride) and the chloride formed separate phases, there would be only one composition of the mixture of oxygen and hydrochloric acid which would permit the permanent co-existence of both phases. If, however, the oxide (or oxychloride) formed a solid solution, the catalyzer would have a different composition corresponding to every mixture of the gases.

We will make no assumption as to the composition of the catalyzer, nor as to its mode of action. We need only assume that when the measurements become concordant and remain so for some time the catalyzer has reached a condition of constant composition.

The first experiments at  $352^{\circ}$  were made with a mixture containing 92.7 mols. of oxygen to 100 mols. hydrochloric acid. After several days preliminary experiments showed that the catalyzer had reached constancy, ten consecutive measurements were made, the results of which are given in Table I. The extent to which the reaction runs may be expressed in various ways. Previous writers have denoted by  $x$  the fraction of the hydro-

chloric acid decomposed, or, in other words, the ratio of free chlorine to total chlorine in the final mixture. We will adopt this nomenclature. The values of  $x$  are given in the third column. The second column shows how long the gas was left in the catalyzing chamber.

TABLE I.

No.	Time in hours.	$x$ .
1.....	1½	0.870
2.....	16	0.872
3.....	1½	0.871
4.....	1½	0.870
5.....	12	0.870
6.....	1½	0.868
7.....	1½	0.867
8.....	5	0.869
9.....	4	0.867
10.....	12	0.871
Average,		0.8695

The preliminary experiments had shown that half an hour was not quite sufficient to establish equilibrium. It will be noticed that Expts. 1, 3, 4, 6 and 7 lasted one and one-half hours each, while the five others lasted from four to sixteen hours each. The average value of  $x$  for the first set is 0.8692, for the second, 0.8698. The close agreement of the two averages indicates that true equilibrium<sup>1</sup> had been reached in every case.

This experiment shows that at 352° this mixture containing 92.7 mols. of oxygen and 100 mols. of hydrochloric acid reacts until 86.95 per cent. of the hydrochloric acid is decomposed, when equilibrium is reached. In the final mixture there would therefore be 100 — 86.95 or 13.05 mols. of hydrochloric acid;  $\frac{1}{2} \times 86.95$  or 43.47 mols. of chlorine; also 43.47 mols. of water vapor; and 92.7 —  $\frac{1}{2} \times 86.95$  or 71.0 mols. of oxygen.

The average pressure in the experiments was very close to one atmosphere. The partial pressures of the four gases must be proportional to the above figures and their sum must equal unity. They are therefore, HCl, 0.0763; Cl<sub>2</sub>, 0.2542; H<sub>2</sub>O, 0.2542; O<sub>2</sub>, 0.4152.

<sup>1</sup> In an experiment of this kind the fact that after a certain time a constant state is reached does not prove beyond question that equilibrium is reached. But this fact and the consistency of the results obtained at different temperatures and concentrations together show pretty conclusively that this is the case.

According to the mass law,

$$\frac{p_{\text{Cl}_2}^{\frac{1}{2}} p_{\text{H}_2\text{O}}^{\frac{1}{2}}}{p_{\text{HCl}} p_{\text{O}_2}^{\frac{1}{2}}} = K,$$

where  $K$  is a constant at any one temperature. Substituting the above values in this equation we obtain for  $K$ , the equilibrium constant at  $352^\circ$ , the value 4.15.

Another series of experiments at  $352^\circ$  was made in a new apparatus with fresh catalyzer. In this case the mixture contained 29.7 mols. of oxygen to 100 mols. hydrochloric acid. After the gas had passed through the apparatus for several days the measurements were begun. It was at once apparent that a longer time was required for the establishment of equilibrium than in the preceding case. Later experiments showed that in general the reaction progresses more slowly the greater the percentage of hydrochloric acid in the original mixture. This fact has also been inferred by Haber<sup>1</sup> from the experiments of Lunge and Marmier.<sup>2</sup> With this mixture at least four hours was allowed for each experiment. Twenty-four experiments lasting, altogether, seven days gave concordant results. The last ten of these may be regarded as the best. They are recorded in Table II.

TABLE II.

No.	Time in hours	$x$
1.....	5	0.810
2.....	12	0.810
3.....	6	0.806
4.....	6	0.802
5.....	5	0.813
6.....	4	0.801
7.....	4	0.816
8.....	10	0.815
9.....	6	0.802
10.....	5	0.808

Average, 0.808

The average pressure in these experiments was 0.93 atmosphere. Calculating as in the preceding case we find,  $K = 3.95$ .

The ratio of hydrochloric acid to oxygen in the final mixture was eleven times as great in this case as in the preceding. A small error in  $x$  is considerably magnified in  $K$ . Considering this fact and the slowness with which equilibrium is attained at this temperature, the agreement between the two values of  $K$  at  $352^\circ$  may be regarded as satisfactory.

<sup>1</sup> Haber: *Thermodynamik technischer Gasreaktionen*.

<sup>2</sup> Loc. cit.

In better agreement were the two series at  $386^{\circ}$  recorded in Tables III and IV. Table V contains the results of a single series at  $419^{\circ}$ . At these temperatures, it will be noted, a shorter time was necessary for establishing equilibrium. In each series the catalyzer had reached a constant state for at least twenty-four hours before the experiments were begun.

TABLE III.

No.	Time in minutes.	$x$ .
1.....	20	0.844
2.....	20	0.844
3.....	30	0.843
4.....	115	0.848
5.....	185	0.845
		<hr/>
		Average, 0.845

Temperature  $386^{\circ}$

Average pressure, 0.98 atmosphere.

Original composition, 327 mols.  $O_2$  to 100 mols. HCl.

TABLE IV.

No.	Time in minutes.	$x$ .
1.....	60	0.803
2.....	840	0.808
3.....	30	0.809
4.....	20	0.809
5.....	30	0.801
6.....	60	0.801
7.....	60	0.797
8.....	60	0.805
9.....	240	0.797
10.....	120	0.806
		<hr/>
		Average, 0.804

Temperature  $386^{\circ}$ .

Average pressure, 0.96 atmosphere.

Original composition, 48.8 mols.  $O_2$  to 100 mols. HCl.

TABLE V.

No.	Time in minutes.	$x$ .
1.....	35	0.819
2.....	55	0.817
3.....	60	0.816
4.....	30	0.824
5.....	30	0.824
6.....	30	0.818
7.....	40	0.824
8.....	10	0.823
9.....	20	0.819
10.....	20	0.820
		<hr/>
		Average, 0.820

Temperature  $419^{\circ}$ .

Average pressure 1.08 atmospheres.

Original composition, 327 mols.  $O_2$  to 100 mols. HCl.

The results of all five series are collected in Table VI. The ratio of oxygen to hydrochloric acid in the final mixtures, given in the fifth column, is not used in the calculations but is given to show the range of the experiments.

TABLE VI.

No. of series.	Temp Degrees.	Average pressure in atmos- pheres.	Mols O <sub>2</sub> to 100 mols. HCl in orig- inal gas.	Mols O <sub>2</sub> to 100 mols. HCl in final gas.	<i>x</i> .	K.
1.....	352	1.00	92.7	544.0	0.869	4.15
2.....	352	0.93	29.7	49.5	0.808	3.95
3.....	386	0.98	327.0	1970.0	0.845	2.94
4.....	386	0.96	48.8	146.0	0.804	3.01
5.....	419	1.08	327.0	1700.0	0.820	2.40

## THERMODYNAMIC CONSIDERATION OF THE RESULTS.

It is evident from the preceding tables that the equilibrium constant, and, for a mixture of given composition, the yield of chlorine, are higher, the lower the temperature. This fact is in accordance both with the observations of previous experimenters and with the demands of thermodynamics for the decomposition of hydrochloric acid by oxygen is accompanied by an evolution of heat. The amount of heat evolved in the reaction may be found from the heats of formation of hydrochloric acid and water.

The various determinations of the heat of formation of liquid water are reviewed in Ostwald's *Lehrbuch*. The three most reliable seem to be those of Schuller and Wartha,<sup>1</sup> of Than,<sup>2</sup> and of Thomsen.<sup>3</sup>

Schuller and Wartha burned hydrogen at atmospheric pressure in an ice calorimeter and obtained for the heat of formation of one mol. of water 68420 small calories.<sup>4</sup>

Than exploded oxygen and hydrogen in a bomb in the ice calorimeter. For 2 grams of hydrogen, 838.6 grams of ice melted. Taking 2.015 grams hydrogen as 1 mol. and using Smith's<sup>5</sup> value for the latent heat of fusion of ice, 79.9 cal., and adding the correction of 970 cal. calculated by Ostwald, we have 68480 cal.

Thomsen in a water calorimeter found 68360 cal. at 18°. This corresponds to 68500 cal. at 0°.

<sup>1</sup> Wied. Ann. 2, 359 (1877).

<sup>2</sup> Ibid. 13, 84 (1881).

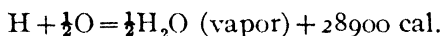
<sup>3</sup> Pogg. Ann. 148, 368 (1873).

<sup>4</sup> This value and all the following include the external work.

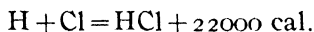
<sup>5</sup> Phys. Rev. 17, 193 (1903).



The mean of these three determinations at  $0^\circ$  is 68470 cal. In order to find the heat of formation of water vapor the heat of vaporization must be subtracted from this quantity. The mean of the three values for the heat of vaporization of 1 mol. of water at  $0^\circ$  given in the tables of Landolt and Bornstein is 10750 cal. From the mean of five determinations of the heat of vaporization at  $100^\circ$ , and from the specific heats of water and water vapor we may calculate the latent heat at  $0^\circ$ . This gives the value 10680 cal. These two values are sufficiently concordant. Subtracting their mean from the heat of formation of liquid water at  $0^\circ$  and then dividing by two we find,

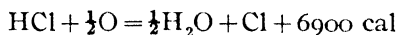


For the heat of formation of hydrochloric acid Thomsen<sup>1</sup> found,



This value is also used by Berthelot, but whether or not he determined it independently I am unable to learn. This value is nearly independent of the temperature.

Subtracting the second of these equations from the first we have



From the best determinations of the specific heats of these four gases it appears that the change in heat capacity during this reaction is zero, within the limits of accuracy of the experimental data. The heat of reaction is therefore independent of the temperature.

The change of the equilibrium constant with the temperature is given by the van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{-Q}{RT^2}, \quad (1)$$

where  $K$  is the equilibrium constant in terms of partial pressures,  $T$  is the absolute temperature,  $R$  is the gas constant and  $Q$  is the total heat evolved when the reaction occurs at constant pressure. If  $Q$  is expressed in calories,  $R = 1.985$ .

When  $Q$  is independent of the temperature, as in the present case, equation (1) is, in its integrated form,

$$\ln K = \frac{Q}{RT} + C'$$

<sup>1</sup> Pogg. Ann. 148, 177 (1873).

where  $C'$  is the integration constant. Substituting the numerical values for  $Q$  and  $R$  and changing from natural to common logarithms, we have,

$$\log K = \frac{1509}{T} + C;$$

$C$  is another constant which can be determined when  $K$  is known for any one temperature. It may therefore be found from each of the five results recorded in Table VI. The average of the five values of  $C$  thus obtained is  $-1.811$ . We have then finally,

$$\log K = \frac{1509}{T} - 1.811 \quad (2)$$

This simple equation permits the calculation of the equilibrium constant of the Deacon reaction at any temperature. In order to show how well the experimental values of  $K$  contained in Table VI agree with theory, I have repeated them in Table VII by the side of the values calculated from equation (2).

TABLE VII.

Temperature. Degrees	K (obs)	K (calc.)
352	4.15	4.02
352	3.95	4.02
386	2.94	3.02
386	3.01	3.02
419	2.40	2.35

## COMPARISON WITH OTHER DETERMINATIONS.

Haber,<sup>1</sup> in his excellent review of the work of Lunge and Marmier, concludes that true equilibrium was established in these experiments at the highest temperature at which they worked,  $480^\circ$ , and from their data he calculates,  $K = 2.0$ . Equation (2) gives 1.56 for this temperature. The discrepancy is doubtless due to the fact that in Lunge and Marmier's experiments at  $480^\circ$  the cupric chloride sublimed from the hot to the cooler part of the tube through which the gases were passing. Therefore the gases came in contact last with catalyzer considerably cooler than  $480^\circ$  and hence gave a larger yield of chlorine than corresponds to equilibrium at that temperature.

Another independent value of  $K$  at a very high temperature may be calculated from the experiments of Löwenstein<sup>2</sup> upon

<sup>1</sup> Loc. cit. p. 168.

<sup>2</sup> Z. physik. Chem. 54, 715 (1906).

the dissociation of water vapor and hydrochloric acid. Thus the dissociation constant of water is,

$$K' = \frac{p_{\text{H}_2}^{\frac{1}{2}} p_{\text{O}_2}^{\frac{1}{2}}}{p_{\text{H}_2\text{O}}}$$

and that of hydrochloric acid is,

$$K'' = \frac{p_{\text{H}_2}^{\frac{1}{2}} p_{\text{Cl}_2}^{\frac{1}{2}}}{p_{\text{HCl}}}$$

Hence  $K$ , the equilibrium constant of the Deacon process, is equal to  $\frac{K''}{K'}$ .

Löwenstein finds at  $1537^\circ$  that hydrochloric acid is 0.274 per cent. dissociated into chlorine and hydrogen. From this we find,  $K'' = 0.00137$ . For water we find from Löwenstein's results,  $K' = 0.0074$  at  $1510^\circ$  and  $K' = 0.0122$  at  $1590^\circ$ . From these, interpolations by means of the van't Hoff equation give for  $1537^\circ$ ,  $K' = 0.0103$ . Dividing this by the above value of  $K''$  we get, for the equilibrium constant of the Deacon process at  $1537^\circ$ ,  $K = 0.133$ .

From equation (2) we find  $K = 0.106$ .

This is a very surprising agreement when we consider that the latter result was obtained by an extrapolation through more than  $1100^\circ$ .

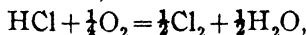
#### THE ELECTROMOTIVE FORCE OF THE HYDROGEN-OXYGEN CELL.

From equation (2) we find for  $25^\circ$ ,  $K = 1800$ . We are now able to calculate the free energy of the Deacon process at  $25^\circ$ .

By a familiar theorem,

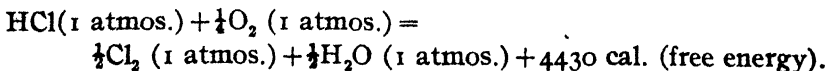
$$A = RT \ln K,$$

where  $A$  is the free energy (exclusive of this work done by the atmosphere) of the reaction,

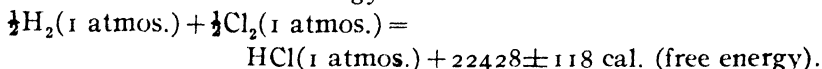


when the gases consumed and those produced are all at atmospheric pressure.

Substituting numerically for  $R$ ,  $T$  and  $K$ , we find  $A = 4430$  cal. We may express this result in the form of an equation similar to those of thermochemistry.

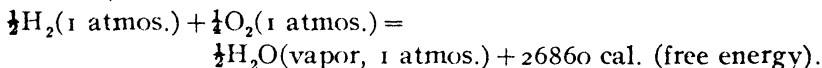


The free energy of formation of hydrochloric acid may be calculated from the work of Dolazalek,<sup>1</sup> who measured the electromotive force between a hydrogen and a chlorine electrode immersed in a hydrochloric acid solution in which the vapor-pressure of hydrochloric acid was determined. The solutions ranged from five to twelve times normal. From Dolazalek's data Haber has calculated the free energy and found



This value is for 30°, but the free energy and the heat of formation (22,000) are so nearly identical that the change of the former with 5° change of temperature is negligible. The same equation is true, therefore, at 25°.

Such free energy equations may be added and subtracted just like those of thermochemistry. Adding the two above equations, we have,



From the free energy of a reaction it is easy to calculate the electromotive force of a cell in which this reaction occurs. In order to change from calories to volts we will use the same factor that Haber used in changing Dolazalek's data from volts to calories, namely 23110. Dividing 26860 by this number we obtain 1.162 volts as the electromotive force which a cell would have if its reaction consisted in the formation from oxygen and hydrogen at atmospheric pressure of water vapor at atmospheric pressure (assuming that it could exist at this pressure at 25°). Now the vapor-pressure of liquid water at 25° is 23.6 mm. of mercury. A cell converting hydrogen and oxygen into liquid water would have an electromotive force higher by  $\frac{RT}{2} \ln \frac{760}{23.6}$ , or, 0.045 volt. We therefore find for the electromotive force of the ordinary hydrogen-oxygen cell, 1.207 volts.

The accuracy of this value depends chiefly upon the accuracy of two data which we have used in the calculation. Error in the experimental determination of the equilibrium in the Deacon process could hardly lead to an error of more than a small fraction of a millivolt in this final result. On the other hand, an error of 200 calories in the value we have chosen for the heat of reaction in the

<sup>1</sup> Z. physik. Chem. 26, 334 (1898).

Deacon process seems quite possible and would produce an error of about 5 millivolts. It is possible too that Dolazalek's results may be far enough from the truth to give a similar error. On the whole, perhaps, we may regard the present determination as entitled to a little less weight than the value obtained in my previous paper,<sup>1</sup> namely,  $1.217 \pm 0.010$  volts.

The agreement between these two values, obtained in absolutely different ways, without a single datum in common, proves conclusively that the generally accepted value is about one-tenth of a volt too low.

At present we may take as the most probable value of the electromotive force of the hydrogen-oxygen cell, 1.212 volts, the average of the two determinations. I intend soon to review both these determinations with the aid of some new data and to compare them with the experiments of Nernst on the dissociation of water vapor and with those of Haber on the oxygen-hydrogen cell at high temperatures.

In conclusion I wish to express my deep obligation to Professor A. A. Noyes for generously placing at my disposal the means of carrying out this investigation in the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

#### SUMMARY.

Apparatus and method are described by which at the desired temperatures the conditions of equilibrium were obtained for the reaction,  $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ .

The catalyzer, cupric chloride, in each series of experiments required several days to reach a constant state, after which concordant results were obtained.

The time necessary to bring the gases to equilibrium was greater the lower the temperature and the smaller the percentage of oxygen present.

Experiments were made at three temperatures,  $352^\circ$ ,  $386^\circ$  and  $419^\circ$ , and over a considerable range of concentration, the ratio of oxygen to hydrochloric acid in the final mixture being forty times as great in one case as in another.

At constant temperature the results are in accordance with the mass law.

The yield of chlorine from a given mixture is greater the lower the temperature, and the change of equilibrium constant with the

<sup>1</sup> This Journal, 28, 158 (1906); Z. physik. Chem., 55, 465.

temperature is in good agreement with the equation of van't Hoff.

A simple equation is given from which the equilibrium constant at any temperature may be calculated.

The value thus calculated for  $1537^{\circ}$  agrees with the results of Löwenstein on the dissociation of water and hydrochloric acid at that temperature.

From the equilibrium constant of the Deacon reaction at  $25^{\circ}$ , and the experiments of Dolazalek, the electromotive force of the hydrogen-oxygen cell at  $25^{\circ}$  is calculated to be 1.207 volts, while the value obtained by an entirely different method in a previous paper was  $1.217 \pm 0.010$  volts.

The conclusion of the previous paper, that the value at present accepted for the electromotive force is one-tenth of a volt too low, is thus fully corroborated.

## LIQUID METHYLAMINE AS A SOLVENT, AND A STUDY OF ITS CHEMICAL REACTIVITY.

BY H. D. GIBBS.

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SINCE Franklin<sup>1</sup> and his co-workers have shown, in an extended series of investigations that liquid ammonia shows many analogies to water, both as a solvent and in its reactions, liquid methylamine would naturally be expected to show the same analogies to methyl alcohol. As  $\text{H.NH}_2$  is to  $\text{H.OH}$  so is  $\text{CH}_3\text{NH}_2$  to  $\text{CH}_3\text{OH}$ . Owing to its intermediate position in the group  $\text{H.NH}_2$ ,  $\text{H.OH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{OH}$ , one would expect methylamine to possess the property of existing in compounds as methylamine of crystallization to a degree corresponding to that of the other members of the group. The compounds in which water is known to be a constituent as water of crystallization are too numerous for mention; ammonia is a constituent of a large number of known compounds as ammonia of crystallization, and methyl alcohol possesses the property of uniting with many compounds as alcohol of crystallization. Among the latter which are mentioned in the literature are:

<sup>1</sup> Franklin and Kraus: *Am. Ch. J.* **20**, 820 and 836; **21**, 1 and 8; **23**, 277; **24**, 83; Franklin and Stafford: *Ibid.* **28**, 83; Franklin and Cady: *This Journal*, **26**, 499; Franklin and Kraus: *Ibid.* **27**, 191; Franklin: *Ibid.* **27**, 802.

$\text{LiCl} \cdot 3\text{CH}_3\text{OH}$ ; <sup>1</sup>  $\text{MgCl}_2 \cdot 6\text{CH}_3\text{OH}$ ; <sup>1</sup>  $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$ ; <sup>2</sup>  $\text{BaO} \cdot 2\text{CH}_3\text{OH}$ ; <sup>3</sup>  $\text{BaO} \cdot 4\text{CH}_3\text{OH}$ ; <sup>4</sup>  $\text{SbCl}_5 \cdot \text{CH}_3\text{OH}$ ; <sup>5</sup>  $\text{CuSO}_4 \cdot \text{CH}_3\text{OH}$ ; <sup>6</sup>  $5\text{NaOH} \cdot 6\text{CH}_3\text{OH}$ ; <sup>7</sup>  $3\text{KOH} \cdot 5\text{CH}_3\text{OH}$ ; <sup>8</sup>  $\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ ; <sup>9</sup>  $\text{CH}_3\text{ONa} \cdot \text{CH}_3\text{OH}$ ; <sup>10</sup> and various methyl alcohol addition products of  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$ ,  $\text{SiF}_4$  described by Kuhlmann.<sup>11</sup> From these analogies it would be expected that many compounds, both organic and inorganic, containing methylamine of crystallization, can be prepared and experimentation has upheld this theory.

With these considerations in view, a study of the solubilities of a number of compounds in liquid methylamine, together with some of the reactions involved and qualitative measurements of the electrical conductivity of the solutions, has been undertaken. The results of quantitative conductivity measurements together with a description of the apparatus employed and a further study of some of the reactions which have not as yet been investigated will be described in later papers.

The liquid methylamine<sup>12</sup> employed in these investigations was the same as that used in the boiling-point determinations<sup>13</sup> and the same steel cylinder was used as a container. This steel cylinder is of about 500 cc. capacity and is fitted with an outlet tube and a tightly fitting needle valve. Methylamine, stored in sealed glass cylinders, is distilled into the steel cylinder, the connections being made by means of lead tubing of 0.5 cm. diameter attached to the glass with sealing-wax and to the steel cylinder by soldering to a steel screw connection made tight with lead washers. The glass tubes of about 100 cc. capacity containing the methylamine are cooled in a Dewar test-tube of liquid

<sup>1</sup> Simon: J. pr. Chem. [2] 20, 374.

<sup>2</sup> Kane: Ann. 19, 168.

<sup>3</sup> Dumas and Peligot: Ibid. 15, 10.

<sup>4</sup> Forcrand: Bull. soc. chim. 46, 337.

<sup>5</sup> Williams: Jsb. 1876, 332.

<sup>6</sup> Forcrand: Bull. soc. chim. 46, 61.

<sup>7</sup> Forcrand: Ann. chim. phys. [6] 11, 462.

<sup>8</sup> Göttig: Ber. 21, 1835.

<sup>9</sup> Forcrand: Ann. chim. phys. [6] 27, 547.

<sup>10</sup> Ibid. [6] 11, 455.

<sup>11</sup> Ann. 33, 208.

<sup>12</sup> Obtained from Kahlbaum through the kindness of the trustees of the Bache Fund, to whom acknowledgments are due.

<sup>13</sup> Gibbs: This Journal, 27, 851.

ammonia and one end is drawn down in the blast flame to about the size of the lead tubing so that when inserted into the lead tubing a snug fit is afforded. A minimum surface of the sealing-wax is thus exposed to the methylamine whose solvent action upon the wax is quite rapid. The steel cylinder is cooled in ice water, the valve opened and the glass tube of methylamine warmed in the air and finally in warm water, thus causing the methylamine to distil into the steel cylinder from which it can be conveniently redistilled into any form of apparatus and in any quantity desired.

The solubilities, qualitative measurements of the electrical conductivity of solutions of various substances in methylamine and the reactions which often take place were studied in closed tubes, the most convenient form of which is shown in Fig. 1.

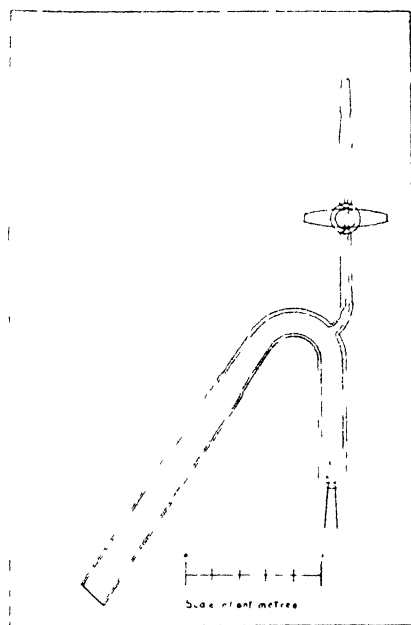


Fig. 1.

Platinum electrodes, sealed into one arm of the tube, are connected to the measuring apparatus by dipping the short platinum wires into mercury terminals. Solids are introduced into the other arm and sealed in. The tube, after exhaustion with the mercury pump is ready to be connected, by means of lead tubing and



sealing-wax, to the methylamine cylinder and the liquid distilled in. In order to permit of quantitative determinations, the tube is weighed after each of the operations described. Methylamine is first condensed in that arm of the tube which contains the electrodes (by cooling the arm in liquid ammonia) so that the electrical conductivity of the liquid can be measured. If any appreciable conductivity is shown, owing to the introduction of impurities, the determination is discontinued and the process repeated with a clean tube and fresh substance. The methylamine is brought in contact with the solid by slowly inverting the tube. If solution is effected, the conductivity is measured after pouring the solution back into the arm containing the electrodes. In the investigation of liquids and gases the tube is first sealed and exhausted and the liquid or gas introduced through the stop-cock. The Kohlrausch form of apparatus with bridge and telephone is employed for the measurements.

Crystallization of the compounds in solution is often effected by cooling the reaction tube in liquid ammonia. The excess of the solvent is in many cases easily and completely removed by spontaneous evaporation on opening the stop-cock. In other cases exhaustion with the mercury pump is necessary to remove traces which are mechanically held. Other substances break down under reduced pressure and give up methylamine which was held in chemical combination. This is especially noticeable in the case of certain aromatic hydroxyl compounds which not only unite with one molecule of methylamine for each hydroxyl group, but also crystallize with additional amounts of methylamine varying with the temperature and pressure. The temperature at which the substances under investigation and the methylamine are brought in contact is frequently an important factor in the character of the reaction. In the majority of the cases investigated the methylamine and other reacting substances were at the room temperature when brought in contact with each other. In many cases the rise of temperature caused by the reaction was sufficient to produce complicated and secondary changes which were not investigated. Quinone and the aldehydes, picric acid and other nitro derivatives are notable examples, and it is very probable that the reactions with these substances will be much simplified if carried on in the cold. Re-

sorcinol and quinol undergo complicated reactions with methylamine if contact occurs at the room temperature, while if the arm of the tube which contains the hydroxyl compound is cooled in liquid ammonia and the methylamine condensed therein, the reactions are quantitative and unaccompanied by the production of by-products.

The gain in weight of the reaction tube will in most cases, except when volatile products are formed as a result of the reaction, show the amount of methylamine which has entered into reaction. It is to be expected that this method of investigation will often give unsatisfactory quantitative results owing to impurities which may be present in the reacting substances and to the fact that in many cases the last traces of methylamine which are mechanically held are difficult of removal, and also it must be remembered that some of the reaction products break down slowly, constantly losing weight and giving up methylamine or other volatile products, and in other cases the reactions are evidently not quantitative. The amounts of methylamine of crystallization are in many cases difficult of determination by analytical methods for the crystals usually have low melting-points, effloresce at low temperatures and comparatively high pressures, and are difficult to obtain uncontaminated by the mother-liquors from which they are crystallized. No attempts to determine the composition of the crystalline compounds thus obtained, have been made by physicochemical methods. Therefore, the amount of methylamine of crystallization in combination, as determined from analytical data, can not in some cases be considered as definitely fixed.

The behavior of the substances under investigation was in each case studied as fully as circumstances at the time seemed to warrant. Some of the observed reactions have been carefully studied, the products recrystallized from other solvents and analyzed. In many instances, however, this has not been attempted, the reactions being manifestly complicated, leading too far afield, and perhaps better attempted as a separate piece of research.

#### EXPERIMENTAL PART.

*The Hydrocarbons.*—All of the hydrocarbons investigated are soluble in liquid methylamine, the solutions are colorless and

practically non-conductors of the electric current.<sup>1</sup> At the temperatures to which the solutions were subjected, namely from the room temperature to that of liquid ammonia (about 20° to about -33°), no evidence of a reaction was apparent.

Acetylene was found to be very soluble. Measured volumes of the gas were conducted into weighed quantities of methylamine. In one case 0.3584 gram of methylamine absorbed 18 cc. of acetylene. Normal pentane, toluene and metaxylene were found to be miscible in every proportion which was tried. Paraffin, triphenylmethane, diphenyl, naphthalene, anthracene and phenanthrene are all very soluble and crystallize readily from the solutions, no methylamine of crystallization being held in any case.

#### THE HYDROXYL COMPOUNDS.

*Methyl alcohol* is miscible in all proportions, the solution is colorless and conducts the electric current to some extent. As the alcohol is an electrolytic solvent it is possible that the conductivity is due to the dissociation of the methylamine. There is no evidence of reaction.

*Isopropyl alcohol* is miscible in all proportions, the solution is colorless and is practically a non-conductor of the electric current. There is no evidence of a reaction.

*Tertiary butyl alcohol* in the solid state dissolves very slowly. Upon raising the temperature above the melting-point of the alcohol (23.5°) the two liquids are found to be miscible in all proportions. The solid alcohol separates slowly when the concentrated solution is cooled. The solutions are colorless and practically non-conductors of the electric current. There is no evidence of a reaction.

*Cetyl alcohol* is very soluble, the solution is colorless and practically a non-conductor of the electric current. The alcohol can be crystallized from the solution. There is no evidence of a reaction.

<sup>1</sup> An arbitrary scale for expressing the results of the conductivity measurements was adopted.

Resistance less than 100 ohms.....very good conductor.

From 100 ohms to 200 ohms.....good conductor.

From 200 ohms to 500 ohms.....fair conductor.

From 500 ohms to 2000 ohms.....poor conductor.

From 2000 ohms to 5000 ohms.....very poor conductor.

Above 5000 ohms.....practically a non-conductor.

The solutions measured were usually quite concentrated and the cell employed was of about unit resistance capacity.

*Glycerol* is very soluble with marked rise of temperature. The solution is colorless and a fairly good conductor of the electric current. There is some evidence of a reaction taking place between the two liquids, although no reaction products were isolated. It is possible that the glycerol contained a little water but the assumption is not necessary to explain the conductivity, for both glycerol and methylamine are electrolytic solvents.

*Hydroxylamine hydrochloride\** is very soluble but was not further investigated.

*Phenol* is very soluble with a slight rise of temperature. The colorless solution which is formed is a good conductor of the electric current. Upon cooling the solution, by means of liquid ammonia, there is slowly formed a fine crop of beautiful colorless crystals. These were purified by allowing the internal pressure to force the mother-liquor out through the stop-cock, after which they were melted, the solution cooled and the crystals allowed to again slowly form and the mother-liquor again removed. By repeating this operation a number of times a crop of crystals was obtained melting from  $8.5^{\circ}$  to  $9.0^{\circ}$ . The methylamine in these crystals was obtained by distillation with caustic potash, collecting the evolved gas in standard hydrochloric acid solution and titrating with standard ammonia solution, using methyl-orange as an indicator.

0.4054 gram substance gave 0.1480 gram methylamine.

$C_6H_5.ONH_3.CH_3.CH_3NH_2$ , calculated  $CH_3NH_2$  39.79, found 36.57.

*Orthonitrophenol\** is very soluble, producing a yellow solution which was not further investigated. The ammonia compound  $NH_4O.C_6H_4.NO_2$  is described by Merz and Ris,<sup>1</sup> and its electrical conductivity in liquid ammonia solution has been investigated by Franklin and Kraus.<sup>2</sup>

*Picric acid* is very soluble with marked rise of temperature. The orange-red solution which is formed is a good conductor of the electric current. Upon expelling the excess of methylamine the solid, as it dries, changes from a deep red to a yellow-orange color. This compound is somewhat soluble in alcohol and very soluble in warm water. The aqueous solution deposits yellow

\* All compounds marked with a star were investigated by Professor E. C. Franklin, and the results here recorded are taken from his unpublished notes.

<sup>1</sup> Ber. 19, 1752.

<sup>2</sup> Am. Ch. J. 23, 295.

crystals on cooling. These crystals were washed with alcohol and dried in a vacuum desiccator. They are not exploded by friction or shock. On heating they gradually turn red at  $186^{\circ}$  and at  $195^{\circ}$  decompose, turning black without melting. The reaction products are under further investigation. An addition product,  $C_6H_2(NO_2)_3OH.NH_2CH_3$  has previously been prepared from aqueous, alcoholic or chloroformic solutions.<sup>1</sup>

*Thymol* is very soluble with a slight rise of temperature. The colorless solution which is formed is a fairly good conductor of the electric current. Upon removing the excess of methylamine with the mercury pump, a process which requires about six hours, some colorless crystals were formed upon cooling the thick viscous solution with liquid ammonia. The melting-point of these crystals is about  $25^{\circ}$ . Attempts to determine their composition gave no satisfactory results.

$\alpha$ -*Naphthol* is very soluble with rise of temperature. The colorless solution is a good conductor of the electric current. The uncombined methylamine is removed by spontaneous evaporation, leaving a thick liquid which solidifies to a mass of colorless crystals on cooling. Melting-point about  $37^{\circ}$ .

0.2360 gram of  $\alpha$ -naphthol retains 0.1042 gram of methylamine.

$C_{10}H_7.ONH_3CH_3.CH_3NH_2$ , calculated  $CH_3NH_2$  30.14 per cent., found 30.60.

This compound gives up a portion of its methylamine under diminished pressure, loses its crystalline form and becomes a white amorphous solid.

0.2360 gram of  $\alpha$ -naphthol retains 0.0504 gram of methylamine.

$C_{10}H_7.ONH_3CH_3$ , calculated  $CH_3NH_2$  17.74 per cent., found 17.60.

$\beta$ -*Naphthol* is very soluble with rise of temperature. The solution which is formed is of a light yellow color, probably due to impurities, and is a good conductor of the electric current. The spontaneous evaporation of the uncombined methylamine leaves a viscous liquid in which no crystals could be induced to grow. At this point, 0.1682 gram of  $\beta$ -naphthol retains 0.0656 gram of methylamine.

$C_{10}H_7.ONH_3CH_3.CH_3NH_2$ , calculated  $CH_3NH_2$  30.14 per cent., found 28.05.

Upon diminishing the pressure this liquid gives up methylamine

<sup>1</sup> Delépine: Ann. chim. phys. [7], 8, 461; Ristenpart: Ber. 29, 2530.

readily until a second comparatively stable condition is reached. At this point still no crystals were obtained.

0.1682 gram  $\beta$ -naphthol retains 0.0337 gram of methylamine.

$C_{10}H_7.ONH_2CH_3$ , calculated  $CH_3NH_2$  17.74 per cent., found 16.7.

It is, of course, possible that the two conditions described do not represent definite compounds. It is probable, however, that crystallization may be effected by means other than those tried. Compounds with aniline,  $C_6H_5NH_2.C_{10}H_7.OH$ , and other allied substances have been produced.<sup>1</sup> Friedländer and Zakrzewski<sup>2</sup> have found that  $\beta$ -naphthylamine is produced on heating  $\beta$ -naphthol with ammonia.

*Quinol* is very soluble with a marked rise of temperature. The solution which is formed is a good conductor of the electric current. When methylamine and quinol react at room temperature the heat developed is sufficient to produce secondary reactions. When the quinol is cooled by immersing the reaction tube in liquid ammonia and the methylamine condensed upon the cold substance the reaction is not accompanied by the formation of secondary products. In the former case the solution is reddish brown, in the latter light pink. From the light pink solution on cooling there is obtained a beautiful crop of pink crystals. The color is probably not that of the pure compound.

0.6022 gram of quinol retains 1.4843 grams of methylamine.

$C_6H_4.(ONH_2CH_3)_2.6CH_3NH_2$ , calculated  $CH_3NH_2$  69.3 per cent., found 71.1.

These crystals melt considerably below the room temperature. When the methylamine is allowed to escape from this liquid another crop of pink crystals separates out.

0.6022 gram of quinol retains 0.3456 gram of methylamine.

$C_6H_4.(ONH_2CH_3)_2$ , calculated  $CH_3NH_2$  36.09 per cent., found 36.4.

These are comparatively stable at room temperature and atmospheric pressure but when the pressure is slightly reduced by suction of the water pump they slowly effloresce. The corresponding aniline addition product  $C_6H_4(OH)_2.(C_6H_5NH_2)_2$  has been prepared by Hebebrand.<sup>3</sup> With the mercury pump these crystals break down into a white solid.

<sup>1</sup> Dyson: J. Chem. Soc. 43, 469.

<sup>2</sup> Ber. 27, 763.

<sup>3</sup> Ibid. 15, 1973.

0.6022 gram of quinol retains at good vacuum 0.1672 gram methylamine.

$C_6H_4.OH.ONH_2CH_3$ , calculated  $CH_3NH_2$  22.02 per cent., found 21.7.

This compound without further purification melts at  $105^\circ$ , assuming a brilliant red color in melting; on cooling, it solidifies into a brilliant red crystalline mass. The compound is very soluble in water, the solution being a good conductor of the electric current. An aqueous solution of quinol is a very poor conductor. The compound is almost insoluble in ether while quinol is soluble. Methylamine is given off upon boiling the aqueous solution with potassium hydroxide solution.

*Resorcinol* behaves in a manner analogous to quinol. It is very soluble with rise of temperature, the solution is a good conductor of the electric current, and the reacting substances must be strongly cooled in order to prevent the formation of secondary products. The solution is light green in color and separates light green crystals on cooling.

0.6755 gram of resorcinol crystallized with 0.8945 gram of methylamine.

$C_6H_4.(ONH_2CH_3)_2.3CH_3NH_2$ , calculated  $CH_3NH_2$  58.5 per cent., found 57.

From other experimental data it seems probable that a compound with a larger amount of methylamine of crystallization is capable of existence. As the methylamine is allowed to escape from the melted crystals, another crop of beautiful light green crystals is formed. These are quite stable at atmospheric pressure and room temperature but not as stable as the corresponding quinol compound.

0.6755 gram of resorcinol retains 0.3542 gram of methylamine.

$C_6H_4.(ONH_2CH_3)_2$ , calculated  $CH_3NH_2$  36.09 per cent., found 34.3.

These crystals give up more methylamine with the mercury pump, producing a white amorphous solid.

0.6755 gram of resorcinol retains at good vacuum 0.1807 gram of methylamine.

$C_6H_4.OH.ONH_2CH_3$ , calculated  $CH_3NH_2$  22.02 per cent., found 21.1.

This compound without further purification melts at  $95^\circ$  to a red liquid which solidifies to brilliant red crystals on cooling.

Methylamine is given off on boiling with caustic potash solution. The corresponding ammonia compound  $C_6H_4.OH.ONH_4$ , has been previously prepared by passing dry ammonia gas into a solution of resorcinol in dry ether.<sup>1</sup>

*Pyrogallol* is very soluble, the solution being a good conductor of the electric current. When the excess of methylamine is allowed to escape at room temperature the product assumes a constant weight but remains a viscous liquid, resisting all attempts to induce crystallization.

0.1608 gram pyrogallol retains 0.1135 gram of methylamine.

$C_6H_3.(ONH_2CH_3)_3$ , calculated  $CH_3NH_2$  42.52 per cent., found 41.4.

Upon exhaustion with the water pump the substance quickly gives up methylamine and assumes the solid state and practically constant weight.

0.1608 gram of pyrogallol retains 0.0763 gram of methylamine.

$C_6H_3.OH.(ONH_2CH_3)_2$ , calculated  $CH_3NH_2$  33.02 per cent., found 32.2.

With the mercury pump the compound gives up an additional very small amount of methylamine, the stable form evidently being that in which two molecules of methylamine are in combination with one of pyrogallol. This compound is very soluble in water and on contact with the oxygen of the air is at once darkened in a manner characteristic of an alkaline solution of pyrogallol. An ammonia compound,  $C_6H_3(OH)_2.ONH_4$ , has been prepared by passing dry ammonia gas into a solution of pyrogallol in dry ether.<sup>2</sup>

*Phenolphthalein* is very soluble, the resulting solution being of a faint pink color and a fair conductor of the electric current. If all traces of moisture are absent from the methylamine and the phenolphthalein, the solution will in all probability be without color. Upon the removal of the excess of methylamine a viscous mass is first formed from which no crystals were induced to grow, and with the mercury pump this dried to a white solid.

0.0854 gram of phenolphthalein retains 0.0160 gram of methylamine.

$C_6H_4C_2O_2.(C_6H_4.ONH_2CH_3)_2$ , calculated  $CH_3NH_2$  16.3 per cent., found 15.79.

<sup>1</sup> Malin: Ann. 138, 80; Baker: Patentschrift des Deutschen Reiches, 40372; Friedländer's "Fortschritte der Theerfarbenfabrication," 1, 564.

<sup>2</sup> Luynes and Esperandien: Ann. Supplement, 6, 252.



The compound dissolves in water, giving a red solution. From previous considerations of the behavior of the hydroxyl ring compounds at ordinary temperatures and below, in the absence of water, it seems quite probable that the methylammonium salt of phenolphthalein is formed. Baeyer<sup>1</sup> has found that a solution of phenolphthalein in aqueous ammonia loses all of its ammonia on drying, while on heating in sealed tubes at 160° to 170°

iminophenolphthalein,<sup>2</sup>  $C \left\{ \begin{array}{l} : (C_6H_4OH)_2 \\ \cdot C_6H_4 \cdot C(NH) \\ \cdot NH \end{array} \right\}$ , is produced. H. Meyer,<sup>3</sup>

by the action of ammonia solutions at about the same temperatures, obtained monoiminophenolphthalein,  $C \left\{ \begin{array}{l} : (C_6H_4OH)_2 \\ \cdot C_6H_4CO \\ \cdot NH \end{array} \right\}$ , as the principal product. In both cases the hydroxyl group remains intact.

*Alizarin* turns a dark purple immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. When liquid methylamine is poured upon the crystals they turn a brilliant dark blue and dissolve, forming an intense purple solution which conducts the electric current to some extent. After the removal of the excess of methylamine by spontaneous evaporation under slightly reduced pressure a solid of a dark red-brown color remains.

0.1091 gram of alizarin retains 0.0286 gram of methylamine.

$C_6H_4 \cdot C_2O_2 \cdot C_6H_2(OH \cdot CH_3)_2$ , calculated  $CH_3NH_2$  20.6 per cent., found 20.8.

This compound is extremely soluble in water, giving a purple-red solution. No attempt was made to prepare the compound containing one less molecule of methylamine,  $C_6H_4 \cdot C_2O_2 \cdot C_6H_2OH \cdot ONH_2CH_3$ , by exhaustion with the mercury pump, but it seems quite probable from the results obtained with quinol and resorcinol that this compound can be obtained. It is probable that the ammonium salt,  $C_{14}H_7O_4 \cdot NH_4$ , has been prepared by Perkin,<sup>4</sup> although no analyses of the compound were made.

<sup>1</sup> Ann. 204, 74.

<sup>2</sup> Baeyer and Burkhardt: Ber. 11, 2297; Ann. 204, 111.

<sup>3</sup> Monatsh. 20, 358.

<sup>4</sup> J. Chem. Soc. 75, 435.

## THE ALDEHYDES.

*Acetic aldehyde* is readily miscible with violent rise of temperature and the discoloration of the liquid. The solution is a fair conductor of the electric current. No reaction products have been isolated.

*Benzaldehyde* is readily miscible with strong rise of temperature. The solution formed is a fairly good conductor of the electric current, due probably to the presence of benzoic acid. Upon distilling off the methylamine, by cooling one leg of the reaction tube in liquid ammonia, the conductivity of the solution rapidly decreases. When the two liquids are again mixed, the temperature again rises and the conductivity returns to the previous figure. After removing the excess of methylamine with the mercury pump and cooling the resulting liquid in liquid ammonia, colorless crystals form very slowly. The composition of the reaction products has not been determined.

*Metanitrobenzaldehyde* is readily soluble with slight rise of temperature. The resulting pink solution is a poor conductor of the electric current. On cooling the solution in liquid ammonia beautiful dark red crystals can be induced to grow. When the excess of methylamine is allowed to escape, the entire solution can be made to solidify into a mass of these crystals which melt quite sharply at  $-9.0^{\circ}$ .

0.1890 gram metanitrobenzaldehyde retains 0.2439 gram of methylamine.

$C_6H_4.NO_2.CHO.6CH_3NH_2$ , calculated  $CH_3NH_2$  55.24 per cent., found 56.3.

Upon exhausting the tube with the mercury pump, another crop of crystals is obtained. These are lighter in color, melt at about  $47^{\circ}$ , at which temperature they also undergo decomposition.

0.1890 gram metanitrobenzaldehyde retains 0.0422 gram of methylamine.

$C_6H_4.NO_2.CHO.CH_3NH_2$ , calculated  $CH_3NH_2$  17.1 per cent., found 18.3.

There is some evidence of an intermediate product lying between the two described.

## THE KETONES AND QUINONES.

*Acetone* is miscible in all proportions and the solution which is formed is to some extent a conductor of the electric current.

The conductivity, however, may be due to the dissociation of the methylamine in the acetone. The evidence of a reaction taking place between the two liquids when in contact for several hours, was very slight.

Götschmann<sup>1</sup> has obtained, by combination of acetone and methylamine on long standing, methyl diacetoneamine,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{NH}(\text{CH}_3)$ . The action of aniline upon acetone in sealed tubes has been studied by Pauly.<sup>2</sup>

*Benzophenone* is quite soluble and readily crystallizable unchanged from the solution, which is a very poor conductor of the electric current.

The action of ammonia upon benzophenone in sealed tubes has been studied by Pauly.<sup>3</sup>

*Benzil* is very soluble with marked rise of temperature. The solution which is formed is a poor conductor of the electric current. Upon the removal of the excess of methylamine a mass of poorly defined yellow crystals is formed which melt at about  $23^\circ$ . These do not give methylamine on boiling with potassium hydroxide solution.

0.2620 gram benzil gained 0.0674 gram in weight.

$(\text{C}_6\text{H}_5)_2(\text{CO})_2\cdot 2\text{CH}_3\text{NH}_2$ , calculated  $\text{CH}_3\text{NH}_2$  20.46, found 22.4.

The reaction which takes place is probably deep-seated. Laurent<sup>4</sup> and others described complicated reactions corresponding to this in ammonia solutions.

*Carbamide* is very soluble without reaction. The compound is readily crystallizable unchanged from the solution, which is a poor conductor of the electric current.

*Quinone* reacts immediately on coming in contact with the vapors of methylamine, turning successively green, purple and black, with evolution of much heat. The solution is of a dark red color and is a fairly good conductor of the electric current. A study of the reaction products has not yet been attempted.

By action of dry ammonia in alcohol, ether and chloroform solutions, various products have been produced.<sup>5</sup> The action of some substituted ammonias with quinone and substitution prod-

<sup>1</sup> Ann. 197, 38.

<sup>2</sup> Ibid. 187, 216.

<sup>3</sup> Loc. cit.

<sup>4</sup> J. pr. Chem. 35, 461; Henius: Ann. 228, 341; Pinner: Ber. 35, 4138.

<sup>5</sup> Waskresensky: Jsb. 26, 801; J. pr. Chem. 34, 251; Knapp and Schultz: Ann. 210, 178; Hebebrand and Zinke: Ber. 16, 1555.

ucts of quinone has also been investigated. By heating quinone with dimethylamine solution tetramethyldiaminoquinone is obtained,<sup>1</sup>  $(N(CH_3)_2)_2C_6H_2O_2$ .

*Anthraquinone* is only slightly soluble with no evidence of reaction and the solution is practically a non-conductor of the electric current.

#### THE ACIDS.

*Acetic acid* is very soluble with strong rise of temperature. The colorless solution which is formed is a good conductor of the electric current. By cooling the solution beautiful colorless crystals which evidently contain some methylamine of crystallization are obtained. At atmospheric pressure they give up methylamine, forming methylammonium acetate which melts at about  $80^\circ$ . This salt is very soluble in water and the solution is a good conductor of the electric current

0.4050 gram acetic acid unites with 0.2091 gram of methylamine.

$CH_3COO.NH_3CH_3$ , calculated  $CH_3NH_2$  34.11, found 34.03.

On heating the methylammonium acetate above the melting-point in sealed tubes a reaction takes place, probably producing methylacetamide,  $CH_3CO.NHCH_3$ ,<sup>2</sup> although the compound was not isolated.

*Phenylacetic acid* behaves in a manner very similar to acetic acid. It is very soluble with strong rise of temperature and the solution is a good conductor of the electric current. From this solution on cooling, beautiful crystals which evidently contain methylamine of crystallization, are obtained. They immediately lose their form upon release of the pressure and give up methylamine, forming methylammonium phenyl acetate.

0.2300 gram phenylacetic acid unites with 0.0545 gram methylamine.

$C_6H_5.CH_2COO.NH_3CH_3$ , calculated  $CH_3NH_2$  18.57, found 19.1.

This salt is very soluble in water and the solution is a good conductor of the electric current.

Beilstein gives no record of the ammonium salt or the methylammonium salt, but the amide  $C_6H_5.CH_2CO.NH.CH_3$  has been prepared.<sup>3</sup>

<sup>1</sup> Kehrman: Ber. 23, 905; Mylius: Ibid. 18, 467.

<sup>2</sup> Prepared previously by Hofmann: Ber. 14, 2729; Franchimont: Rec. trav. chim. 2, 121.

<sup>3</sup> Ergänzungs. II, 814 (1903).

*Palmitic acid* is very soluble and the solution is a fair conductor of the electric current.

0.1140 gram palmitic acid unites with 0.0136 gram methylamine.

$C_{15}H_{31}COO.NH_3CH_3$ , calculated  $CH_3NH_2$  10.81, found 10.66.

This salt melts at about the same temperature as palmitic acid, namely  $62^\circ$ , is quite soluble in water and is decomposed by caustic potash solution.

*Succinic acid* reacts immediately on contact with methylamine with evolution of much heat. The reaction products are insoluble in the liquid.

0.6207 gram succinic acid unites with 0.3290 gram of methylamine.

$C_2H_4(COONH_3CH_3)_2$ , calculated  $CH_3NH_2$  34.12, found 34.6.

The methylammonium succinate is very hygroscopic, begins to decompose at  $130^\circ$  and gradually assumes a quiet state of fusion at  $150^\circ$ . On cooling, the liquid solidifies to a mass of colorless crystals. The composition of this crystalline substance was not determined.

Methylsuccinimide has been prepared by Menshutkin<sup>1</sup> by the distillation of the salt of succinic acid and methylamine.

*Tartaric acid* (*d*) reacts immediately on contact with methylamine with the evolution of much heat. The reaction products are insoluble in the liquid.

0.8328 gram tartaric acid unites with 0.3474 gram of methylamine.

$C_2H_2(OH)_2(COONH_3CH_3)_2$ , calculated  $CH_3NH_2$  29.19, found 29.43.

The methylammonium tartrate melts, probably with decomposition, at about  $148^\circ$ . It is so very hygroscopic that the salt is soluble in the smallest amount of water and cannot be again dried in a vacuum desiccator over sulphuric acid. Methylamine bitartrate is described by A. Ladenburg<sup>2</sup> as melting and decomposing at  $170^\circ$  with the production of two stereoisomeric methyl tartrides. The racemic variety was also prepared by Wende.<sup>3</sup>

*Benzoic acid* is very soluble with rise of temperature. The solution is a very good conductor of the electric current. Upon

<sup>1</sup> Ann. 182, 92.

<sup>2</sup> Ber. 29, 2710.

<sup>3</sup> Ibid. 29, 2719.

removing the excess of methylamine with the mercury pump a white solid is obtained.

1. 0.3487 gram of benzoic acid unites with 0.0803 gram methylamine.

2. 0.5320 gram of benzoic acid unites with 0.1452 gram methylamine.

$C_6H_5.COO.NH_2CH_3$ , calculated  $CH_3NH_2$  20.27, found I, 18.7; II, 20.9.

The methylammonium benzoate is a very hygroscopic white solid, very soluble in methyl alcohol, ethyl alcohol and insoluble in ether. It is decomposed on heating at atmospheric pressure into benzoic acid and methylamine. Heated in a sealed tube it melts at 110–112°. The affinity for water is so great that the wet salt cannot be dried in a vacuum desiccator over sulphuric acid.

Methylbenzamide,  $C_6H_5.CO.NH.CH_3$ , has been prepared but not from methylammonium benzoate.<sup>1</sup>

*Orthonitrobenzoic acid* is very soluble with rise of temperature. The solution is a good conductor of the electric current. When the temperature of the reacting substances is allowed to rise it is quite probable that the nitro group also enters into the reaction. When the temperature is maintained at a low point only the carboxyl group reacts with the methylamine, forming the methylammonium salt. This salt crystallizes from the concentrated solution in beautiful pale yellow needles.

0.7460 gram of orthonitrobenzoic acid retains on the mercury pump 0.1420 gram of methylamine.

$C_6H_4.NO_2.COONH_2CH_3$ , calculated  $CH_3NH_2$  16.69, found 16.0.

These crystals are very soluble in water, methyl alcohol, ethyl alcohol and insoluble in ether. They can be crystallized readily from a mixture of alcohol and ether. Without further purification they melt from 128° to 129°.

*Phthalic acid* forms methylammonium phthalate upon contact with methylamine. The salt is insoluble in the liquid, very soluble in water, from which solvent it crystallizes in beautiful colorless crystals which decompose easily upon heating.

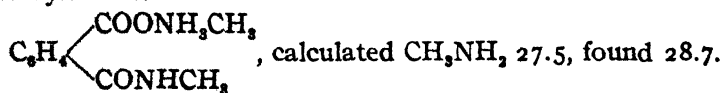
0.3535 gram of phthalic acid unites with 0.1446 gram of methylamine.

$C_6H_4.(COO.NH_2CH_3)_2$ , calculated  $CH_3NH_2$  27.2, found 29.0.

<sup>1</sup> Beilstein: 2, 1159 (1896).

*Phthalic anhydride* reacts with the production of much heat and the resulting compound is insoluble in the liquid.

0.2122 gram of phthalic anhydride retains 0.0855 gram of methylamine.



The methylammonium methylphthalamate, which probably is produced, is very soluble in water and from the solution beautiful, colorless, transparent, star-shaped crystals slowly form.

Methylphthalimide,<sup>1</sup>  $\text{C}_6\text{H}_4(\text{CO})_2\text{NCH}_3$ , has been prepared from phthalic anhydride and methylamine.

*Uric acid* reacts with methylamine and the product, a white powder, is insoluble in the liquid.

0.1354 gram uric acid combines with 0.0225 gram methylamine.

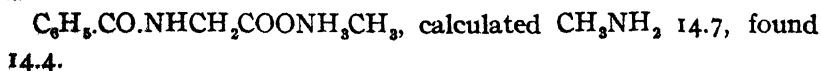


The methylammonium urate is soluble in warm water and decomposes on heating without melting. The methylamine in combination was determined by distillation with caustic potash, the distillate collected in N/10 hydrochloric acid.

0.0919 gram methylammonium urate required 4.15 cc. acid to neutralize the distillate. This is equivalent to 14.03 per cent. of methylamine.

*Hippuric acid* is very soluble with slight rise of temperature. The solution is a good conductor of the electric current. As the excess of methylamine escapes, crystals of methylammonium hippurate are formed.

0.3341 gram of hippuric acid unites with 0.0564 gram methylamine.



The salt is very soluble in cold water and the solution is a good conductor of the electric current.

#### THE HALOGEN SUBSTITUTION PRODUCTS.

*Chloroform* is miscible in all proportions and a reaction gradually sets in between the two liquids in the cold. The conductivity of the solution slowly increases as the reaction proceeds. At higher temperatures it is very probable that the reaction will be

<sup>1</sup> Graebe and Pictet: Ann. 247, 302.

more rapid. On spontaneous evaporation of the solution on a watch-glass the isocyanide odor is very marked. A very hygroscopic residue remains which becomes crystalline on standing in a vacuum desiccator over sulphuric acid. These crystals are probably methylammonium chloride, for they decompose with caustic potash, giving the odor of methylamine and with silver nitrate show the presence of the chlorine ion. The most probable reaction is  $\text{CHCl}_3 + \text{CH}_3\text{NH}_2 = \text{CH}_3\text{NC} + 3\text{HCl}$ , the hydrochloric acid uniting with methylamine to produce methylammonium chloride.

*Ethylene bromide* is miscible but not in all proportions. A reaction slowly commences and becomes very violent unless the reaction tube is kept in a cooling mixture. The products are soluble in liquid methylamine and the solution is a very good conductor of the electric current. From the concentrated solution a mass of beautiful colorless crystals, resembling the cubical crystals of sodium chloride, is obtained on cooling. They are found to be extremely hygroscopic and cannot be recrystallized from aqueous solution. They are insoluble in dry ether and are purified by repeated washing with this solvent and drying with the mercury pump. During the washing, which is conducted in the reaction tube, all air must be excluded, for traces of moisture are sufficient to spoil the form of the beautiful crystals. The melting-point,  $179^\circ$ , is not as sharp as might be desired.

0.9052 gram of substance was dissolved in 200 cc. of water and aliquot parts taken for analysis. The base was set free with caustic potash solution and collected by distillation. The bromine was determined by precipitating and weighing as silver bromide.

I. 1/10 of 0.9052 gram required 7.12 cc. N/10 hydrochloric acid.

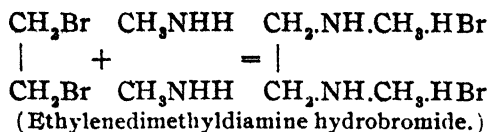
II. 1/10 of 0.9052 gram required 7.14 cc. N/10 hydrochloric acid.

Calculated for  $(\text{CH}_2\text{NH.CH}_2\text{HBr})_2 \cdot \text{Br}$ , 63.91. Found: Br, 64.27 and 64.37.

Calculated for  $(\text{CH}_2\text{NH.CH}_2\text{HBr})_2$ ,  $(\text{CH}_2\text{NH.CH}_2)_n$ , 35.26. Found:  $(\text{CH}_2\text{NH.CH}_2)_n$ , 34.68 and 34.78.

The reaction which takes place is probably best represented by the equation:





The hydrochloride of this base has been prepared by Schneider<sup>1</sup> by heating dimethylethylenedibenzenesulphamide with hydrochloric acid. He states the boiling-point of the base to be 119°, and the melting-point of the hydrochloride to be 235-236°.

*Brombenzene* is miscible and the solution is a non-conductor of the electric current. If any reaction takes place, it goes on so slowly, at room temperature and below, as to be imperceptible. The brombenzene can be separated unchanged by distilling off the methylamine.

*Parabromacetanilide* is very soluble without reaction and separates unchanged from the concentrated solution, which is a poor conductor of the electric current.

#### THE NITRO COMPOUNDS.

*Nitromethane* is miscible, a slight rise of temperature resulting. The solution is a fairly good conductor of the electric current. On cooling in liquid ammonia colorless crystals are formed. By blowing off the mother-liquor, melting the crystals and recrystallizing seven different times they melt quite sharply from -8.0° to -7.5°. Analysis was made by distilling with potassium hydroxide and collecting the distillate in N/10 hydrochloric acid.

0.5439 gram of substance gave 0.2050 gram of methylamine.

$\text{CH}_3\text{NO}_2\text{.CH}_3\text{NH}_2$ , calculated  $\text{CH}_3\text{NH}_2$  33.7, found 37.8.

It would be expected from this method of production that the crystals would be contaminated by some free methylamine.

*Nitrobenzene* is miscible, producing an intense dark red solution, with a slight rise of temperature. The solution is to a small extent a conductor of the electric current. In all probability no reaction takes place at the temperatures studied.

*Metadinitrobenzene* is very soluble. Immediately upon contact with methylamine vapor the compound turns a beautiful purple and as the solvent distils into the tube a brilliant, reddish purple solution is formed. The solution is a good conductor of the electric current. On concentrating the solution, crystals of metadinitrobenzene separate out and these resume their original color as the methylamine evaporates. There is no evidence of a

<sup>1</sup> Ber. 28, 3072.

reaction. The brilliantly colored solution is in all probability due to dissociation in the electrolytic solvent.

The behavior of dinitrobenzene in liquid ammonia is somewhat analogous and has been studied by Franklin and Kraus.<sup>1</sup>

*Orthonitrotoluene*\* is very soluble. The solution is slightly yellow.

*Dinitrotoluene*\* (2-4) is very soluble. The solution is blue in color, greenish in thin layers.

*Dinitraniline* (1-2-4) is not affected by the methylamine vapor but in the liquid the crystals immediately turn a brilliant red and quickly go into solution. The brilliant red solution is a good conductor of the electric current. The original substance crystallized unchanged from the solution.

*Trinitraniline* (1-2-4-6) melts on contact with the vapor of methylamine with evolution of heat and formation of a dark red mass. The dark red solution which is formed is a good conductor of the electric current. From the concentrated solution, brilliant red crystals are formed. The reaction which evidently goes on has not been further investigated.

#### THE SUGARS.

*Galactose* is quite soluble, a slight rise of temperature resulting. The solution is a poor conductor of the electric current. Upon the removal of the excess of methylamine a viscous mass, which becomes solid on standing, results.

0.2440 gram galactose retains with the mercury pump at good vacuum 0.0775 gram of methylamine.

$C_5H_{11}O_6CHO.2CH_3NH_2$ , calculated  $CH_3NH_2$  25.3, found 24.1.

The reaction products have not been investigated.

*Glucose* behaves in a manner quite analogous to galactose; however, the viscous mass obtained after removal of the methylamine, crystallizes quite well on standing.

0.4520 gram of glucose retains on the mercury pump 0.1023 gram of methylamine.

$C_5H_{11}O_6CHO.2CH_3NH_2(?)$ , calculated  $CH_3NH_2$  25.3, found 18.4.

The reaction products have not been investigated.

*Sucrose* is quite soluble, a slight rise of temperature resulting. The solution is to a slight extent a conductor of the electric current. There is some evidence of a reaction but the question has not been sufficiently investigated.

<sup>1</sup> Loc. cit.

## MISCELLANEOUS COMPOUNDS.

*Acetamide* is very soluble without reaction. From the solution, which is a fairly good conductor of the electric current, the compound is readily crystallizable.

*Phenyldiazine* is miscible in all proportions and there is no evidence of a reaction. The solution is to some extent a conductor of the electric current.

*Amyl formate* is miscible in all proportions. The sample employed was evidently contaminated with a small amount of formic acid and therefore no definite conclusions can be drawn as to the conductivity of the solution.

*Pyridine* is miscible in all proportions without reaction. The solution is a non-conductor of the electric current.

*Azobenzene* is very soluble. From the brilliant red solution, which is a non-conductor of the electric current, the azobenzene crystallizes beautifully. There is no evidence of a reaction.

*Diphenylketoxime* dissolves almost immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. The solution is to a small extent a conductor of the electric current. The more dilute solutions seem to be better conductors than the concentrated. From the concentrated solution beautiful colorless crystals are obtained.

0.5246 gram diphenylketoxime retains with the mercury pump at good vacuum 0.0850 gram of methylamine.

$(C_6H_5)_2CNOH.CH_3NH_2$ , calculated  $CH_3NH_2$  13.62, found 13.94. This compound decomposes a few degrees below  $140^\circ$ , giving off methylamine and leaving the oxime which melts at  $140^\circ$ . A further study of the composition of the compound was not made.

*Benzenesulphimide* is very soluble with reaction. The resulting solution is a good conductor of the electric current. On the removal of the excess of methylamine on the mercury pump only a semi-solid mass results, from which no crystals are obtained. The reaction was not further studied.

*Metanitrobenzenesulphonamide* is quite soluble and the colorless solution is a good conductor of the electric current.

## DYES.

*Gallein* turns a brilliant blue immediately upon contact with methylamine vapor, a strong rise of temperature resulting. The reaction products are only slightly soluble in the liquid, pro-

ducing a bluish purple solution which is a poor conductor of the electric current. Upon removal of the excess of methylamine with the mercury pump 0.2891 gram of gallein holds 0.0814 gram of methylamine.

$C_{20}H_{12}O_7 \cdot 3CH_3NH_2$ , calculated  $CH_3NH_2$  20.5, found 21.7.

The resulting solid is, by reflected light, a very dark purple.

It is evident that the carboxyl group will unite with one molecule of methylamine, and, judging from the behavior of other hydroxyl ring compounds such as phenol, quinol, resorcinol and pyrogallol, when two hydroxyl groups are united to the same ring only one uniting with methylamine to form a stable compound, a second molecule of methylamine is accounted for by combination with the ring holding the two hydroxyl groups. The third molecule can easily be held by the hydroxyl group or the quinone oxygen of the other ring as both have been found to be reactive. The reaction products, have, however, not been investigated in order to verify this theory.

*Coerulein* is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a poor conductor of the electric current.

0.1635 gram of coerulein retains with the mercury pump 0.0272 gram of methylamine.

$C_{20}H_{10}O_6 \cdot 2CH_3NH_2$ , calculated  $CH_3NH_2$  15.2, found 14.8.

The resulting solid is, by reflected light, a very dark green.

The arguments used in the case of gallein concerning the character of the reaction, hold equally well here.

*Dichlorgallein* turns a brilliant blue immediately upon contact with methylamine vapor. The brilliant blue solution which is formed with the liquid is a very poor conductor of the electric current. The reaction which takes place is more complicated than the reaction between methylamine and gallein. The product which holds about 23 per cent. methylamine has not been investigated.

*Tetrachlorgallein*<sup>1</sup> turns a brilliant blue immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. The reaction products, which are only slightly soluble

<sup>1</sup> My thanks are due to Professor William R. Orndorff, of Cornell University, for the samples of gallein, coerulein, dichlorgallein and tetrachlorgallein, which are the same as those employed by Orndorff and Brewer in their investigation of the constitution of these compounds. Am. Ch. J. 26, 97.

in liquid methylamine, form a blue solution which is a poor conductor of the electric current. The reaction product holds over 25 per cent. of methylamine, is very soluble in water and does not contain the chlorine ion. No further study of the reaction has been made.

*Indigo* is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a good conductor of the electric current. There is no evidence of a reaction, for the indigo separates unchanged from the concentrated solution.

*Methyl orange* is to a small extent soluble. The resulting deep red solution is a moderately good conductor of the electric current. There is no evidence of a reaction as the original substance separates unchanged upon opening the reaction tube and allowing the methylamine to escape.

*Rosaniline* turns a dirty brown color immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. This compound is very soluble in the liquid and the resulting dirty brown solution is to a slight extent a conductor of the electric current.

#### INORGANIC COMPOUNDS.

The solubilities of a number of inorganic compounds have been investigated by Franklin<sup>1</sup> but the reactions which occur in many cases have been investigated in only a few instances. For the most part the sulphates of the metals are insoluble in liquid methylamine, while the nitrates and the halogen salts are about equally divided.

*Aluminum chloride\** is insoluble.

*Arsenious iodide\** is very soluble.

*Ammonium chloride\** is very soluble.

*Bismuth nitrate\** is insoluble.

*Bismuth chloride\** is very soluble with the separation of a white mass. Probably a basic salt analogous to Franklin's ammono basic salts<sup>2</sup> is formed.

*Boric acid\** is slightly soluble with slow reaction, producing an amorphous mass which is presumably the methylammonium salt.

<sup>1</sup> All of the data on the inorganic compounds, with the exception of silver nitrate, methyl mercuric chloride, mercuric cyanide, mercuric chloride, mercurous chloride and mercuric iodide, have been taken from his unpublished notes.

<sup>2</sup> This Journal, 27, 826.

*Cadmium iodide*\* unites with methylamine to form a bulky, white mass which is insoluble, or only slightly soluble in the liquid.

0.1096 gram of cadmium iodide unites with 0.0369 gram of methylamine.

$\text{CdI}_2 \cdot 4\text{CH}_3\text{NH}_2$ , calculated  $\text{CH}_3\text{NH}_2$  25.31, found 25.26.

*Calcium chloride*\* unites with methylamine, forming a bulky mass which is insoluble.

*Cuprous chloride*\* reacts, producing an unpromising mass which was not investigated.

*Cupric sulphate*\* forms an intensely blue mass which is insoluble.

*Chromic chloride*\* is slightly soluble, forming with an excess of the solvent a purple mass which is an addition product.

*Iodic acid*\* is insoluble.

*Lithium chloride*\* is very soluble, forming a viscous solution which solidifies to a crystalline mass on cooling.

*Lithium nitrate*\* is very soluble. On standing, the contents of the tube solidify to a crystalline mass.

*Lead nitrate*\* forms a bulky addition product with the evolution of heat.

*Mercuric chloride* unites with the solvent with evolution of heat and the formation of a white addition product which is only slightly soluble in the liquid. The solution is a poor conductor of the electric current.

*Mercurous chloride* blackens in the methylamine and a mass of crystals separates out on cooling.

*Methyl mercuric chloride* is quite soluble at room temperature but on cooling crystals separate out, the solution almost completely solidifying. The solution is a very good conductor of the electric current.

*Mercuric cyanide* is very soluble with evolution of heat. The colorless solution which is formed is a fair conductor of the electric current. On cooling, crystals are formed in the solution.

*Mercuric iodide* is very soluble. The colorless solution which is formed is a very good conductor of the electric current. An addition product,  $\text{HgI}_2 \cdot \text{XCH}_3\text{NH}_2$ , crystallizes out as a white solid on cooling. Composition not determined.

*Mercurous nitrate*\* blackens on contact with the liquid and goes into solution.

*Potassium bromide*\*, *chlorate*\* and *chromate*\* are insoluble.

*Potassium permanganate*\* is very soluble.

*Silver nitrate* is extremely soluble with considerable rise of temperature. There is at first a blackening of the silver nitrate, and fine black particles are seen suspended in the liquid. These disappear as the concentration decreases, the liquid becoming clear and colorless. The colorless solution which is formed is an excellent conductor of the electric current. When the excess of methylamine is allowed to escape upon opening the stop-cock, a heavy viscous liquid results. Upon cooling this liquid it completely solidifies to a mass of colorless needle crystals which melt at about the temperature of the room.

0.9005 gram of silver nitrate crystallizes with 0.6283 gram of methylamine.

$\text{AgNO}_3 \cdot 4\text{CH}_3\text{NH}_2$ , calculated  $\text{CH}_3\text{NH}_2$ , 42.2, found 41.1.

When the pressure is reduced, these crystals immediately lose their form, giving up methylamine and turning green in color. When the vacuum is fairly good with the mercury pump there still remains held 0.3704 gram of methylamine.

$\text{AgNO}_3 \cdot 2\text{CH}_3\text{NH}_2$ , calculated  $\text{CH}_3\text{NH}_2$ , 26.8, found 29.1.

This substance upon standing continues to give up methylamine. Under the microscope it is seen to have a crystalline structure, the crystals being of a green color or contaminated by impurities which give them the green cast. The crystals are decomposed by water, going partially into solution and leaving a dark brown residue which is soluble in ammonia solution. The crystals are soluble in potassium cyanide solution, insoluble in dry ether and quite soluble in absolute alcohol. On heating they fuse and then explode, giving the isocyanide odor very strongly and leaving a residue of metallic silver.

*Silver sulphate*\* is insoluble.

*Sodium nitrate*\* is very soluble.

*Sodium sulphite*\* is insoluble.

*Sodium thiosulphate*\* reacts with the solvent.

*Tetramethylammonium iodide*\* is insoluble.

*Thallium chloride*\* is insoluble.

#### SUMMARY.

Liquid methylamine has been found to be a remarkably good solvent for organic compounds, exceeding liquid ammonia and

perhaps exceeding methyl alcohol,<sup>1</sup> while for inorganic compounds it is not as good a solvent as liquid ammonia, far inferior to water and ranking perhaps closer to methyl alcohol. It is extremely reactive with both organic and inorganic compounds, in this respect, probably, exceeding the most reactive of the other three solvents mentioned, namely liquid ammonia.<sup>2</sup>

Next to its wide solvent action the most striking property of liquid methylamine is its remarkable power of uniting with many compounds, both organic and inorganic as methylamine of crystallization. Among those mentioned in the literature are:  $\text{LiCl} \cdot \text{CH}_3\text{NH}_2$ ,<sup>3</sup>  $\text{LiCl} \cdot 2\text{CH}_3\text{NH}_2$ ,<sup>3</sup>  $\text{LiCl} \cdot 3\text{CH}_3\text{NH}_2$ ,<sup>3</sup>  $\text{LiCl} \cdot 4\text{CH}_3\text{NH}_2$ ,<sup>4</sup>  $\text{ZrCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ ,<sup>5</sup>  $\text{ThCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ ,<sup>5</sup>  $\text{PbCl}_4 \cdot 4\text{CH}_3\text{NH}_2$ ,<sup>5</sup>  $\text{AgCl} \cdot \text{CH}_3\text{NH}_2$ ,<sup>6</sup>  $\text{AgBr} \cdot \text{CH}_3\text{NH}_2$ ,<sup>6</sup>  $\text{AgI} \cdot \text{CH}_3\text{NH}_2$ ,<sup>6</sup>  $2\text{AgI} \cdot \text{CH}_3\text{NH}_2$ ,<sup>6</sup>  $\text{CH}_3\text{NH}_2 \cdot \text{H}_2\text{O}$ ,<sup>7</sup> and  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH} \cdot \text{CH}_3\text{NH}_2$ .<sup>8</sup>

Addition products other than those already described in the literature, which in all probability contain methylamine of crystallization, have been prepared from phenol, quinol, resorcinol,  $\alpha$ -naphthol,  $\beta$ -naphthol (?), metanitrobenzaldehyde, galactose (?), acetic acid, phenylacetic acid, diphenyl ketoxime, nitromethane, bismuth chloride, cadmium iodide, calcium chloride, cuprous chloride (?), cupric sulphate (?), chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercuric chloride, mercurous chloride (?), methyl mercuric chloride, mercuric cyanide (?), mercuric iodide and silver nitrate.

This work was commenced at Stanford University at the suggestion of Professor E. C. Franklin, and carried to its present state of completion under his kindly advice, direction and assistance.

<sup>1</sup> Liquid methylamine probably does not exceed liquid ammonia as a solvent for organic compounds to the same extent as methyl alcohol exceeds water for the same purpose.

<sup>2</sup> This has often been observed in the case of aqueous and alcoholic solution of ammonia and methylamine. Lassar-Cohn, "Applications of Some General Organic Reactions," page 36. Laubenheimer: Ber. 11, 1155; A. Hempel: J. pr. Chem. [2] 41, 161; Kehrmann and Messinger: Ibid. [2] 46, 565; Bettenhausen-Marquardt, Schulz, Patentschrift des Deutschen Reiches, 72, 253; Paal and Sprenger: Ber. 30, 62; Ristenpart: Ibid. 29, 2526.

<sup>3</sup> Bonnefoi: Compt. rend. 127, 516.

<sup>4</sup> Ibid. 124, 771.

<sup>5</sup> Matthews: This Journal, 20, 826.

<sup>6</sup> Jarry: Compt. rend. 124, 964; Ann. chim. phys. [7] 17, 376.

<sup>7</sup> Henry: Private paper; Beilstein; Ergänzungsab. 1, 596.

<sup>8</sup> Delépine: Ann. chim. phys. [7], 8, 461.



tance. I am grateful to him for the many favors shown me. The manuscript was in process of preparation at the time of the San Francisco fire, and a small portion of the work cannot be chronicled here, owing to the destruction of the notes. As opportunity offers, the research will be extended.

FOOD LABORATORY OF THE  
SAN FRANCISCO HEALTH COMMISSION,  
May 15, 1906.

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[CONTRIBUTION FROM THE COMMITTEE ON PURITY OF REAGENTS, NO. I.]  
**SOME SOURCES OF IMPURITIES IN C. P. CHEMICALS.<sup>1</sup>**

BY J. W. SCHADE

Received June 30, 1906

THE elimination of impurities in chemically pure chemicals has long been the desire of chemists; but owing to a seeming indifference on their part, the manufacturers have not exerted themselves to make their products better than they deemed absolutely necessary to meet the demands. During the past year or two much increased interest has been manifested in the movement to secure the best grade of laboratory reagents consistent with economy in manufacture. To ask for a reagent "absolutely pure" is to ask, in most cases, for the impossible in economical manufacture. The object of this paper is to present some sources of impurities in chemical reagents and to point out that there are limits of purity obtainable by manufacturers.

With few exceptions all reagents are shipped in glass containers. The dry salts probably do not take up impurities from the bottles, but acids and ammonia after standing in containers for a few days are contaminated with impurities from the glass. These impurities may be one or more of the following: iron, potassium, sodium, silica, calcium and from bottles of Jena or "Nonsol" glass, zinc. In the case of ammonia, silica is the principal impurity from the glass; in the case of acids, iron. The latter is due mainly to the fact that small chips of iron oxide flake from the blowpipes used by the glassblowers and although acid is allowed to stand in the bottles before they are washed for use, there are undoubtedly minute particles that escape immediate solution. Acids shipped in carboys having glass covers secured by zinc rings are liable to contamination from the zinc, owing to the

<sup>1</sup> Read at the Ithaca Meeting of the American Chemical Society.

splashing of the acid into the neck of the carboy. Hydrofluoric acid shipped in lead carboys takes up that metal as an impurity. The nature of these impurities is such that the liability of contamination cannot be entirely removed, though it may be diminished by the use of more resistant glass and of glass stoppered carboys.

The second source of impurities is in the chemical works. It is the vessels in which the chemicals are manufactured. These vessels—tanks, stills, condensers, crystallizing dishes, and so on—are made or lined with lead, silver, copper, iron, aluminum, nickel, zinc, platinum, porcelain, earthenware, or glass. The impurities from this source are the metals of which the vessels are made, and from the non-metallic receptacles silica, sodium, potassium, calcium and iron. Iron vessels give rise to other impurities than iron, notably manganese. In the manufacture of sodium bismuthate, for instance, iron vessels cannot be used, owing to the contamination of the product with manganese which, of course, is inadmissible in that reagent. Nickel is found in the best grades of caustic alkalies from the dishes in which they are made. Copper, aluminum, or silica are found in acetic acid from the condensers used in the distillation. Lead tanks are very generally used, especially for crystallizing organic acids such as tartaric and citric. The author has also found it in hydrofluoric acid, ammonium chloride, potassium sulphate, and sodium chloride. The amount of impurities of this class is minimized by the judicious selection of vessels to meet the needs of each case. As with the first class, however, the liability to contamination cannot be entirely removed.

There is another class of impurities introduced during the purification of the salts. These impurities are reagents used to precipitate certain foreign substances or the salts formed by the reaction. For instance, the author once analyzed a sample of sodium chloride in which sulphate had been precipitated by means of barium chloride. This salt gave decided tests for both barium and sulphate, an anomalous condition often met in testing reagents. Another example of this is the presence of calcium in ammonium oxalate. Samples of ammonium oxalate giving clear solutions sometimes contain some hundredths of a per cent. of calcium though the solution from which the crystals were obtained was alkaline. It is evident from these facts that the so-

called "insoluble precipitates" are dissolved to an appreciable extent by the concentrated solutions from which the salts are crystallized.

The final class of impurities includes those occurring in the original source of the chemicals, *i. e.*, in the minerals, and in those substances used in manufacture. These impurities will vary in number and kind, depending on whether the treatment of the mineral is simple or complicated. Sometimes it is impossible for the manufacturer to get rid of certain impurities without putting a prohibitive price on an article. Iron, alumina, and silica, appear in all but the highest-priced grades of caustic alkalies and alkali carbonates. Nickel and cobalt cannot be entirely separated on the large scale cheaply. As has been pointed out above, calcium cannot be entirely removed from ammonium oxalate, strange as it may seem, without considerable trouble and expense. Again, strontium sulphate will not precipitate barium from a solution of strontium chloride or nitrate unless a large excess is added, in which case sulphate is introduced as an impurity. Here the manufacturer is compelled to choose the lesser of two evils. This is the inevitable alternative in many instances.

Calcium persists in barium salts and if considerable calcium is present in the mineral from which the barium is obtained, it is no easy matter to remove it. The removal of iron from copper sulphate is not as simple as one would imagine. Some of the "iron-free" copper sulphate sold on the market contains several thousandths of a per cent. of iron. To separate the two iron must be in the ferric condition. Hydrogen peroxide is theoretically an ideal oxidizing agent in that it introduces no impurity into the copper sulphate, but in practice, nitric acid works somewhat better. Here is a case in which nitric acid is introduced as an impurity in preference to iron. Lead is sometimes found in copper salts and is difficult to remove from the chloride and nitrate. Ferric salts always contain free acid, fused magnesium chloride always contains ammonia, and caustic alkalies and alkali carbonates, as has been said, almost always contain iron, alumina and silica.

These illustrations serve to show that at ordinary prices chemical reagents must be limited in purity. This, however, is not a serious difficulty except in cases when extraordinarily accurate work is to be performed; and the manufacturer can supply at a reasonable

price reagents that will give accurate results when put to the ordinary uses.

LABORATORY OF THE J. T. BAKER CHEMICAL CO.,  
PHILLIPSBURG, N. J., June 28, 1906.

## THE CLASSIFICATION OF COALS.<sup>1</sup>

BY S. W. PARR.

Received July 3, 1906.

THE fundamental properties of coal are directly involved in the decomposition products which are in evidence as a result of geological processes. These products have certain characteristics which manifest themselves in practical every-day use under the two notions of behavior and quality. A scheme of classification, therefore, to have any intelligent significance should be an expression of these two ideas. But while it should be susceptible of practical or commercial interpretation, it should have for its fundamental and ultimate basis, correct analytical facts and scientific data. The methods of classification thus far proposed have seemed to the writer deficient in one or the other of these two phases: either they were devised wholly with industrial ends in view and gave little heed to scientific considerations or they were too profoundly scientific to be capable of translation into any every-day meaning. The work here outlined has been done in connection with the State Geological Survey of Illinois and the effort has been made to embody both of these phases in the consideration of the topic.

The scheme of classification at present most widely recognized is that proposed by Frazer.<sup>2</sup> It has the merit of being intelligible from the industrial standpoint. It does not, however, embody certain phases that seem desirable if any meaning attaches to our discussion of the essentials from a scientific basis as above set forth. Indeed in his recent admirable defense of this classification,<sup>3</sup> Frazer recognizes the lack of data which at the present time would be embodied in the ordinary results of proximate analysis.

It is proposed by Campbell<sup>4</sup> to base a classification on the ratio of the total carbon divided by the total hydrogen. The argument

<sup>1</sup> Read at the Ithaca Meeting of the American Chemical Society.

<sup>2</sup> Trans. Am. Inst. Min. Eng. 6, 430.

<sup>3</sup> Bull. Am. Inst. Min. Eng. March, 1905.

<sup>4</sup> Report of Coal Testing Plant, U. S. Geol. Survey, St. Louis, Professional Paper U. S. G. S. No. 48, Part I, pp. 156-173.

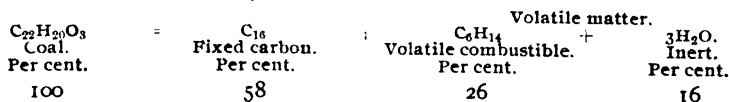
for the use of the total hydrogen in such a ratio seems illogical and at variance with all the facts attending the property of coals. Especially is this true at the lignitic end of the series. Certain it is that the hydrogen there has a different meaning from what it has at the semi-bituminous end. To include the hydrogen of the moisture is to build on a variable that would make it impossible for any one else to reproduce the classification who could not duplicate the exact method of sampling and transmission. With the finely drawn distinctions in the resulting ratios a sample of coal might fall into as many different classes as there were analysts who examined it. It fails also to make use of one valuable fact developed by the usual method of proximate analysis, and that is, the relation of the volatile hydrocarbons to the total carbonaceous material. This, it would seem, comprises such fundamental properties, both with reference to its chemical structure as well as its performance in actual use, that no system of classification could have much value that ignores it. These objections all become accentuated when samples approach the lignitic type. It does not seem possible that these divisions can be properly considered without taking into account the factor for combined water, the "residual cellulose," if we may so designate it. On this point again we quote from Frazer:<sup>1</sup> "It may well be that other factors than carbon and hydrogen will some day furnish the means of a further differentiation of lignites, brown coals, peats and cannel coals."

It is certain that in any careful study of the composition, especially of bituminous coals and lignites, there is truly another factor which seems to have been entirely ignored or overlooked and it is this factor which seems to be primarily the one to be made use of for further differentiating between not only the various sorts of bituminous coals, but especially between the bituminous coals and lignites, as well as between the lignites themselves. Reference has already been made to this constituent, which is the "water of hydration" or that part of the volatile matter which is non-combustible or inert, so far as fuel value is concerned. There is no part of the ordinary proximate analysis that refers to it and its only recognition so far seems to be in that part of Dulong's formula which represents the available hydrogen as consisting

<sup>1</sup> Bull. Am. Inst. Min. Eng. March, 1906, pp. 244-245.

of  $H - \frac{O}{8}$ , which in reality means the total hydrogen less the hydrogen required to combine with the oxygen of the coal. But here again this particular factor is obscured for the reason that the usual ultimate analysis combines in its factors the ordinary moisture as well as this water of composition, and it seems to be not altogether an easy matter to establish a recognition of this constituent of coal as a part of the volatile matter which should receive separate mention and report.

Another difficulty in the case has been the almost universal use of the term "volatile combustible" for "volatile matter," when as a matter of fact, it is not strictly a volatile combustible for the reason that in average bituminous coal approximately one-third of the volatile matter is really non-combustible. This may be further illustrated by putting into molecular form the pure coal of an average bituminous sample, considered as free from moisture and ash, as follows:



This type molecule represents an actual example of Illinois coal and the right-hand member of the equation represents the percentage constituents of the products resulting from destructive distillation. It is not, of course, intended that these formulas represent actual compounds.

Now the point here made is that the two last constituents which are ordinarily reported as "volatile combustible," or still worse as "volatile carbon," are in fact composed of volatile hydrocarbons and hydrogen which are combustible and an inert constituent consisting essentially of hydrogen and oxygen in the proportion to form water, and hence designated as the inert portion of the volatile matter.

Furthermore, if we examine a lignite in the same way, we shall find the proportion of inert volatile matter much greater than in the case of bituminous coals and similarly, the semi-bituminous type will be found to have relatively less of this constituent.

The method of classification herein proposed, therefore, makes prominent use of that part of the volatile matter which has been variously designated as inert or non-combustible, or as "water of composition."

But still another factor even more fundamental must be taken into the account. It has already been referred to as the fact of chief value developed by the process of proximate analysis; this is the ratio existing between the forms of carbon. The amount of fuel constituent which assumes the volatile condition is as much a scientific item as it is a matter of practical importance. This is best expressed in the form of a ratio or percentage and while it may be argued that one ratio is as good as another, a thorough examination of the one here employed will bear out the argument that it best expresses that feature of the composition of coal which recognizes a certain percentage of the fuel as of the volatile sort.

The ratio thus employed is designated by the expression  $vc \times \frac{100}{C}$

in which "vc" is the volatile carbon unassociated with hydrogen, and "C" is the total carbon as determined by analysis.

Briefly outlined, the plan of classification proposes to retain the old nomenclature but to base the first or fundamental divisions upon the ratio  $vc \times \frac{100}{C}$ . Upon applying this principle it

will be found that coals in general divide themselves first into two distinct classes. Those of the anthracitic and those of the bituminous type. In the first division (of the one hundred coals tabulated), no carbon ratio as above expressed is found greater than 15 per cent. In the second division, no carbon ratio falls below 20 per cent. This certainly has the virtue of differentiating between these two types in a manner which demands respectful consideration for this suggested ratio. As to further classification, also, this ratio seems to be all that is needed to differentiate among the members of the first general division. Three main classes are thus indicated: First, anthracites proper with a ratio of  $vc \times \frac{100}{C}$  of less than 4; second, semi-anthracites with ratios falling between 4 and 8; and third, semi-bituminous with ratios grouping very closely around 10 and 12, but in no case exceeding 15.

In the second general division, designated as the bituminous type, we have again three general classes. But here there enters into the account the factor for the inert portion of the volatile matter. Moreover, in order to make one coal comparable with





One further subdivision is necessary: the bituminous group is large and is susceptible of further separation. These subclasses are designated for the present by the letters A, B, C, and D. A and B have the characteristic of a lower percentage of volatile carbon, using that term correctly, with a "fat" and a "lean" feature as indicated by the percentage of inert volatile matter, being from 5 to 10 per cent. under A, and from 10 to 15 per cent. under B. In exactly the same way C and D are characterized by having a high ratio of volatile carbon but sub-class C has the lower percentage of inert volatile matter, thus allying it closely with the cannels or gas coals, and D has the higher percentage of inert matter, thus bringing it nearer the lignites.

Before illustrating this method of classification by tabulating a series from analytical data, one point further should be discussed. That is the element of intrinsic value or relative merit. This enters slightly into the expression for the carbon ratios, but a coal with a high percentage of its fuel content in the fixed form may still be inferior in fuel content to one with a high ratio of volatile combustible.

So also something more of relative value is expressed by the percentage of inert volatile matter but this factor alone should not be made to carry the burden of indicating the grade. Concerning the element of worth it should not dominate in the idea of classification, and in the scheme here proposed this feature is considered as having been given its due weight by arranging particular coals in their ultimate classes in the order of their fuel ratios. Here again is proposed something of an innovation in the use of terms. If we recognize the true fuel of a coal to be all comprised in the total carbon, available hydrogen, and the sulphur, then the reciprocal of the sum of these percentages expressed in hundreds will be a fuel ratio that indicates directly the number of pounds of that particular coal required to make one hundred pounds of true combustible or "fuel," and to avoid confusion of terms, we designate this factor as the "gross coal index." For example, a West Virginia coal has carbon 78.31 per cent., hydrogen 4.31 per cent., and sulphur 0.90 per cent.;

total fuel 83.5 per cent. Then the gross coal index =  $\frac{100}{0.835}$  or 120, which means that 120 pounds of this coal would be required to make 100 pounds of actual fuel. Or again illustrating by a

sample of Dakota lignite: if we have carbon 52.66 per cent., hydrogen 1.83 per cent., and sulphur 2.02 per cent., total 56.51 per cent., the expression for the gross coal index would be  $\frac{100}{0.565}$  or 175, which means that 175 pounds of this material would be required to make 100 pounds of true combustible matter.

In the following table, use is made of the analytical results as obtained at the United States Geological Survey Coal-Testing Plant at St. Louis. The ultimate order of the samples is arranged according to their fuel ratios as above described, while the location in the respective classes is determined by the carbon ratios and the inert volatile percentages as already outlined.

It may be said in conclusion that the analytical results from fifty coals by Lord and Haas previously made<sup>1</sup> and by Williams<sup>2</sup> have been subjected to the same method of classification with equally satisfactory results.

## CLASSIFICATION OF COALS, ST. LOUIS TESTING PLANT, FIRST REPORT.

*Anthracites.*

$$vc \times \frac{100}{C} \text{ below 4 per cent.}$$

*Semi-Anthracites.*

$$vc \times \frac{100}{C} \text{ between 4 and 8 per cent.}$$

Arkansas No. 5 . . . . .	4.66
Arkansas No. 2 . . . . .	7.96

*Semi-Bituminous.*

$$vc \times \frac{100}{C} \text{ from 10 to 15 per cent.}$$

	Carbon ratio, $vc \times 100/C$ .	Gross coal index.
West Virginia No. 10 . . . . .	11.63	110.0
West Virginia No. 6 . . . . .	13.26	113.0
West Virginia No. 7 . . . . .	10.68	113.5
West Virginia No. 11 . . . . .	10.55	120.0
West Virginia No. 5 . . . . .	11.06	120.0
Arkansas No. 3 . . . . .	11.41	123.0
Arkansas No. 1 . . . . .	10.00	124.5

<sup>1</sup> Trans. Am. Inst. Min. Eng. Vol. XXVII.

<sup>2</sup> Mich. Geol. Report, Vol. VIII.

## BITUMINOUS.

## CLASS A.

vc X 100/C 30 to 32 per cent.			
Inert volatile matter 5 to 10 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
West Va., No. 9 ...	21.02	8.46	118.5
West Va., No. 8 ...	25.18	7.78	119.0
West Va., No. 5 ...	21.46	6.33	120.0
West Va., No. 4 ...	20.89	8.03	120.0
West Va., No. 1 ...	29.30	9.53	120.0
Kansas, No. 5 ...	23.54	8.75	120.5
West Va., No. 3 ...	23.30	8.22	123.0
Kansas, No. 3 ...	25.80	7.51	127.0
Kansas, No. 4 ...	28.02	7.97	129.5
Kansas, No. 1 ...	26.69	8.27	131.5
Kentucky, No. 4 ..	29.63	9.73	134.0
Kansas, No. 2 ...	24.56	7.88	136.5

## BLACK LIGNITES

vc X 100/C 27 per cent. and above.			
Inert volatile matter 16 to 20 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
N. Mexico, No. 1 ...	27.10	16.88	147.0
Montana, No. 1 ...	28.77	18.25	153.5
Colorado, No. 1 ...	29.60	19.19	155.0
Wyoming, No. 2 ...	32.36	17.00	160.5
Wyoming, No. 1 ...	32.27	19.99	161.0
N. Mexico, No. 2 ..	33.29	16.18	164.0

## CLASS B.

vc X 100/C 20 to 27 per cent.			
Inert volatile matter 10 to 15 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
Kentucky, No. 1 ...	27.11	10.54	120.0
Alabama, No. 1 ...	25.56	10.51	130.0
Alabama, No. 2 ...	25.27	12.77	135.0
Illinois, No. 3 ...	22.50	11.75	137.0
Iowa, No. 1 ...	24.74	10.08	142.0
Illinois, No. 6 ...	21.50	14.83	146.5
Iowa, No. 5 ...	25.66	13.84	150.0

## CLASS C

vc X 100/C 32 to 44 per cent			
Inert volatile matter 5 to 10 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
Missouri, No. 4 ...	38.61	7.41	121.0
West Va., No. 2 ...	32.16	9.44	121.5
Missouri, No. 1 ...	32.05	9.53	145.5

## BROWN LIGNITES

vc X 100/C 27 per cent. and above.			
Inert volatile matter 20 to 30 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
Texas, No. 2 ...	30.00	23.90	165.0
N. Dakota, No. 2 ...	28.40	23.79	172.0
N. Dakota, No. 1 ..	36.17	21.09	175.0
Texas, No. 1 ...	44.20	22.39	180.0

## CLASS D.

vc X 100/C 27 to 44 per cent.			
Inert volatile matter 10 to 15 per cent.			
Carbon. Ratio.	Inert vol. matter	Gross coal index.	
Indian Terr., No. 2 ...	30.35	11.53	130.0
Indian Terr., No. 3 ...	29.86	11.36	132.5
Indian Terr., No. 1 ...	28.34	11.86	132.5
Kentucky, No. 2 ...	31.59	11.91	133.0
Kentucky, No. 3 ...	29.64	11.76	135.0
Indiana, No. 2 ...	32.09	11.44	140.5
Iowa, No. 3 ...	35.68	11.23	141.0
Indian Terr., No. 4 ..	30.54	13.46	141.5
Illinois, No. 1 ...	33.73	12.77	143.5
Illinois, No. 4 ...	28.30	13.41	145.5
Iowa, No. 2 ...	30.85	12.56	145.5
Indiana, No. 1 ...	31.40	12.00	146.5
Iowa, No. 4 ...	32.70	11.93	147.0
Illinois, No. 5 ...	29.90	14.15	154.0
Missouri ...	30.63	12.12	155.0
Missouri, No. 3 ...	28.61	13.05	162.0
Illinois, No. 2 ...	32.96	12.95	163.0
Indian Terr., No. 5 ...	29.28	13.44	168.0

## AN IMPROVED COLORIMETER.

BY WILLIAM GABB SWEATON.

Received July 5, 1906.

THE instrument permits an accurate comparison of the heights of two columns of liquid enclosed between parallel glass plates. Reflectors consisting of a ground glass plate superposed over a plate of opal glass, are adjusted to project parallel rays from the source of light (Welsbach) vertically through the solutions under investigation.

The solutions are contained in glass cylinders of approximately 33 mm. inside diameter and 100 mm. height, ground plane at the bottom and closed by a plate of the best mirror glass. Each cylinder carries a side arm and stand-pipe near the bottom. During a series of measurements the side arm is connected with a reservoir containing the solution in question, which permits the introduction of any quantity of solution into the cylinder. The latter is placed in a brass sheath to shut off horizontal light. Sheaths and cylinders are fitted in grooves on a metal plate which has circular openings 32 mm. in diameter for the transmission of the light and adjustment of a float cylinder.

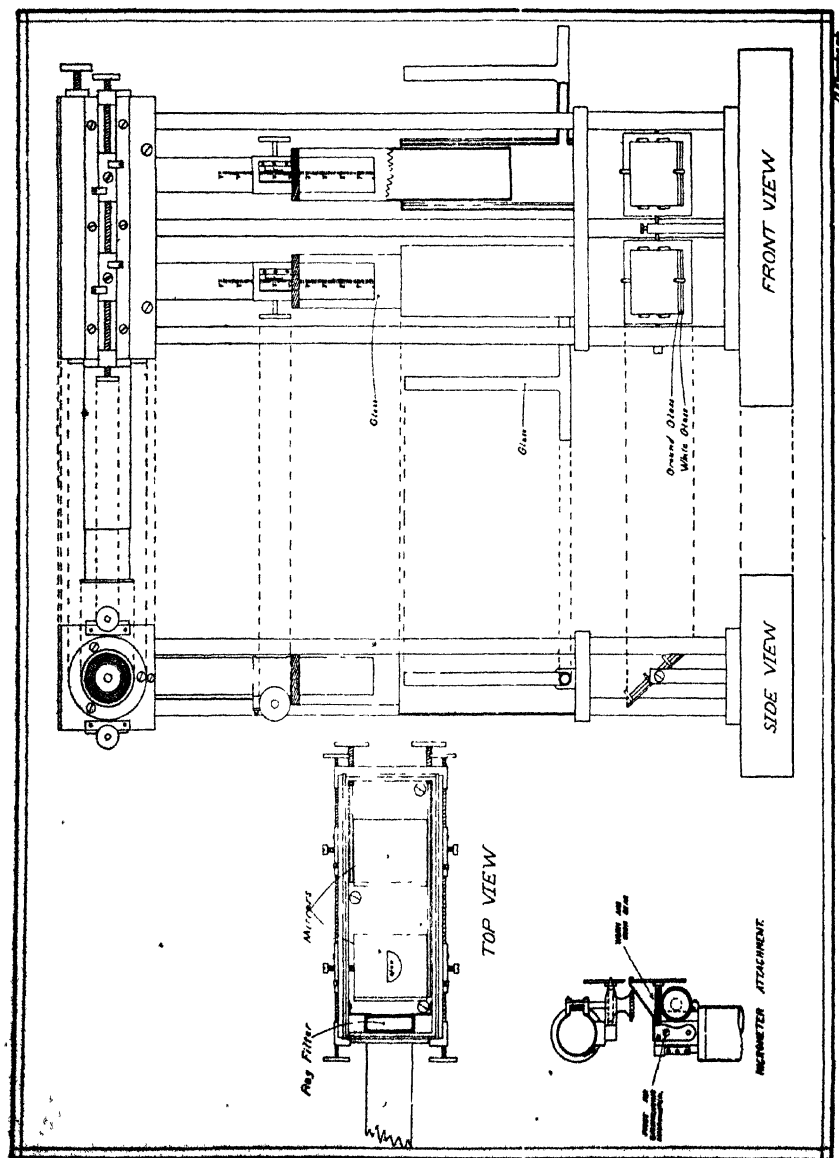
The height of the liquid column is adjusted by a glass float cylinder, 30 mm. in outside diameter, 110 mm. long, ground plane at the bottom and closed also by a plate of the best mirror glass. This cylinder is movable vertically over a brass tube by means of a rack and pinion. It is adjusted so that the two glass plates of the respective cylinders are exactly parallel.

The brass tubes are 22 mm. in external diameter and 125 mm. long. They are permanently attached to a metal plate and have a millimeter scale reading upwards. A vernier indicating 0.1 mm. is riveted to a short brass tube which carries the pinion. To the lower edge of this brass tube the glass float is cemented.

The upper part of the apparatus consists of a box riveted to the metal plate to which the brass tubes are attached. The inside measurements are: width, 45 mm.; height, 47 mm.; length, 130 mm. At one end projects a telescope tube with a total length of 175 mm. when drawn out. The orifice is a pinhole and diaphragms of suitable dimensions may be attached to the inner end of the draw-tube.

The light passing vertically through the solution impinges on

plane glass mirrors above the openings of the brass tubes and is deflected horizontally through the telescope tube. By means of a series of springs these mirrors can be adjusted in three planes. A portion of the silver coating of the mirror next to the telescope



tube is removed, thus giving passage to the beam from the rear mirror. The principle is therefore that of the Donnan colorimeter. The form and dimensions of the silver surface removed will be a matter of personal choice. I have tried many different forms and prefer to use the instrument as a half-shade apparatus, diaphragming the field to about 5 or 6 mm. diameter. When desirable a light filter is used to increase the delicacy of observation.

Measurements are made by comparing the solution in question with some standard. The millimeter scale and vernier are used when the height of the liquid column is several centimeters. To permit accurate comparisons with solutions only a few millimeters in height a simple micrometer, reading 0.01 mm., has been devised. This attachment is thrown into service by a pivot and can be released when not needed.

A high degree of accuracy can be attained if the eye has been trained to make color comparisons for several weeks. In working with various copper- and nickel-ammonia complexes I have repeatedly checked observations to 0.1 mm. The micrometer attachment has been devised only recently and consequently I am not yet in a position to state the ultimate delicacy of the observations recorded with this instrument.

The apparatus has a compact form, as is evident from the diagram. It is, moreover, inexpensive. As a substitute for the etched scale on the brass tube a paper scale such as is provided with galvanometers might be used. It is necessary, of course, to calibrate both the millimeter scale and the micrometer. For very accurate measurements a zero reading is made with each determination by lowering the float cylinder until the two glass plates are in contact, the scale having such a range that this zero reading is always positive.

ANN ARBOR, June 18, 1906.

## ANTIMONY IN BABBITT AND TYPE METALS.

BY H. YOCKEY.

Received July 23, 1906.

IN the May number of this Journal a paper by the author of this article appeared describing the analysis of Babbitt metal as practiced in this laboratory. Antimony was described as being determined by the method of Walters and Apfelder. Since appearing, a number of objections to this method have been received

by me and from such well-known chemists that I could not ignore them, so I determined to try to better the method if I could. The following method is the result of these experiments. By this method antimony can be determined accurately in alloys containing tin and antimony; lead and antimony; lead, tin and antimony; tin, copper and antimony; lead, tin, copper and antimony; and lead, copper and antimony. In these alloys the copper never exceeded 7 per cent. What would be the results with a high copper content, I have not determined.

**Treat** 1 gram filings with 1 gram potassium iodide, 40 cc. water and 40 cc. concentrated hydrochloric acid (sp. gr. 1.2), and boil gently one hour. Filter on asbestos in a Gooch crucible, washing five or six times with hot dilute hydrochloric acid (1:10).

Wash the precipitate and asbestos into a 150 cc. beaker with a little wash-water, and add 20 or 25 cc. concentrated hydrochloric acid and a few crystals of potassium chlorate. Cover with a watch-glass and warm gently, stirring occasionally.

When the antimony is in solution dilute to 100 cc. and filter the asbestos out, washing until the wash-water shows no hydrochloric acid. Boil vigorously five minutes to free the solution from free chlorine. Cool to room temperature, add 1 gram of potassium iodide in solution and titrate the liberated iodine with a standard thiosulphate solution.

The following results were obtained by this method. The alloys were all made from new commercially pure metals by myself.

	Taken Per cent	Found	
		Per cent	Per cent.
1. Pb.....	54.	....	....
Sn.....	22.	....	....
Sb.....	22.	21.95	22.08
Cu.....	2.	....	....
2. Pb.....	45.42	....	....
Sn.....	40.14	....	....
Sb.....	14.44	14.57	14.46
Cu.....	....	....	....
3. Pb.....	76.	....	....
Sb.....	24.	24.12	23.91
4. Pb.....	43.	....	....
Sn.....	50.	....	....
Sb.....	6.5	6.45	6.45
Cu.....	0.5	....	....
5. Pb.....	84.	....	....
Sb.....	15.	15.03	15.12
Cu.....	1.	....	....

The last example I give is the result on an alloy sent me by the Pittsburg Section of the American Chemical Society for analysis. The alloy contained, as reported to me after I had sent in my report, the following: 4.98 to 5.02 per cent. copper, 14.70 per cent. antimony, and the balance tin. My report by this method was 14.73 per cent. antimony, the average of two determinations.

NATIONAL LEAD CO.,  
CINCINNATI BRANCH

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## THE ETCHING TEST FOR SMALL AMOUNTS OF FLUORIDES.

BY A. G. WOODMAN AND H. P. TALBOT

Received July 31, 1906

IN THE course of some work on the detection of fluorides in malt liquors it was found necessary to make a study of the etching test on glass as commonly employed, both from its standpoint as a qualitative test and with a view to making it approximately quantitative.

As a qualitative test, the etching method was found eminently satisfactory, as regards delicacy and reliability, if carried out under proper conditions. The procedure employed was the same in principle as that proposed by Blarez,<sup>1</sup> later modified by Leach,<sup>2</sup> and adopted as a provisional method by the Association of Official Agricultural Chemists.<sup>3</sup> It may be described briefly as follows: To 150 cc. of the liquid to be tested add 10 cc. of potassium sulphate (33 grams per liter), heat the solution to boiling and while boiling add slowly from a burette or pipette 10 cc. of a 10 per cent. barium acetate solution. Continue the boiling for a moment and then set the beaker aside for the precipitated barium sulphate and fluoride to settle. In most cases, unless the precipitate settles very readily, it is preferable to let it stand over night. The clear supernatant liquid is decanted, the precipitate transferred to a filter, washed and ignited in a platinum crucible. An alternative method which is more rapid and has the added advantage of avoiding the use of filters, is to decant off the clear liquid and wash the precipitate into one of the tubes of a centrifugal machine. The sedimented material is then washed directly into a platinum

<sup>1</sup> Chem. News, 91, 39 (1905).

<sup>2</sup> Ann. Rept. Mass. State Board Health, 1905.

<sup>3</sup> U. S. Dept. Agr., Bur. Chem., Circular 28.



crucible. This is placed in the centrifugal machine and whirled again, after which the precipitate can be ignited over a flame.

Meanwhile a small glass plate, clear and free from scratches, is thoroughly cleaned and coated on one side with a mixture of equal parts paraffin and carnauba wax. This can readily be done by pouring a little of the melted wax on the warmed plate. If the excess is drained off and the glass held level, a thin uniform wax coating will result. While the coating is still warm make a characteristic mark, such as a small cross (+), in the wax with a pointed instrument, taking care that the glass is laid bare but not scratched. The precaution should be taken to have the cross of approximately the same size in the different tests; for example, with arms about 4 mm. long and 1 mm. wide. On the uncoated side of the plate locate the cross by marks placed at the ends of the arms with a diamond or file.

To the precipitate in the crucible add 2 to 3 cc. of concentrated sulphuric acid, hold the crucible in the tongs, and heat its upper edge cautiously and quickly in a small flame. Press the glass plate quickly down on the warm crucible, having the cross nearly in the center, and hold it a moment to seal the glass securely to the crucible. The crucible should be embedded in the wax so firmly that it can be lifted by the plate. Support the crucible in a piece of heavy asbestos board in which a hole has been cut so that the crucible fits closely, put two or three drops of water on the glass plate and press down on it a condenser, the lower end of which is closed by a piece of thin sheet rubber such as is employed by dentists. Heat the crucible for an hour by a small flame about 9 mm. long placed 6 mm. below the bottom of the crucible. At the end of this time remove the plate, scrape off the wax and clean the glass on both sides, with "bon-ami" or other polishing material which will not scratch the glass. Examine it by reflected light for an etching. A test should not be considered positive unless the cross can be seen when viewed from either side of the glass.

Several times during the hour it may be necessary to put a drop of water on the plate around the edge of the condenser, to keep the wax from melting.

It is hardly necessary to speak of the need for using the purest reagents obtainable and testing them carefully by blank tests. The barium acetate has given the most trouble from traces of fluorides and it has been found best to prepare it from recrystallized

barium nitrate by precipitating with ammonium carbonate, dissolving the washed carbonate in acetic acid, and recrystallizing the barium acetate.

The condenser may be made from a piece of wide glass tubing arranged so that a constant current of cold water may be kept flowing through it and with a piece of thin sheet rubber (dental dam), stretched tightly over the bottom. The diameter of the tube should be somewhat greater than that of the platinum crucible. A "carbon funnel," as shown in the figure, has been found to answer well.

The electric stove, as recommended by Leach, has not given good results in our hands for furnishing a uniform source of heat, it being our experience that different stoves, and even different sides of the same stove, vary considerably in temperature. On account of the larger surface radiating heat it is more difficult to prevent the melting of the wax than when the small flame is used.

The delicacy of the procedure above described, as tested on aqueous solutions of potassium fluoride, is rather surprising. A perfectly distinct etching is readily obtained from 150 cc. of solution containing 1:10,000,000 of fluorine, and by careful working it is possible to get a recognizable test from 1:50,000,000. By a recognizable test is meant one which is visible from either side of the glass and does not have to be brought out by breathing on the glass. Care should be taken to clean the glass with "bon-ami" before examining it, since sulphuric acid alone will give a "stain" which can be brought out by breathing on it, and might easily be mistaken for an etching. The scouring will always remove this, however.

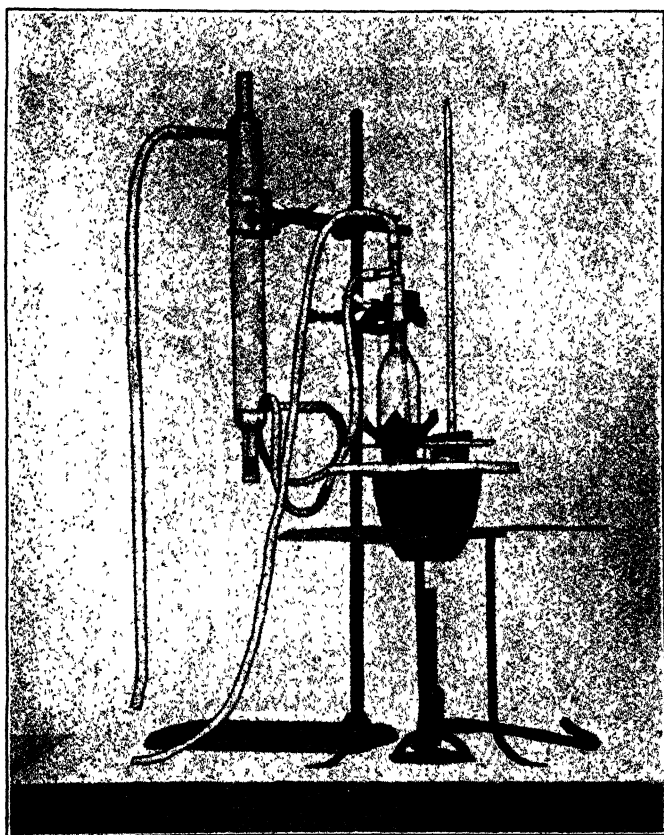
It has been found best to continue the heating for at least an hour. The etching obtained with a small amount of fluorine, say 1:5,000,000, is distinctly less after fifteen or thirty minutes than if the heating is continued for the longer period. There seems to be, however, no advantage in prolonging the test above an hour.

It is best to have the area of glass exposed approximately the same in different tests, because the intensity of the etching produced evidently depends somewhat upon the area of glass exposed. Tests made with 1:100,000 of fluorine showed that a test in one case indicating apparently 25 or 30 times as much fluorine as in another could be obtained by simply exposing that much more glass. The presence of organic matter or of traces of

water during the etching does not seem to make much difference except in the character of the mark obtained. In the absence of organic matter, and when the contents of the crucible are perfectly dry, the resulting etching is usually a "matt" etching, resembling ground glass. If moisture is present, either originally or resulting from the action of organic matter on the sulphuric acid, the etching is clear and transparent and somewhat more difficult to detect.

It was noticed early in the investigation that the test would not infrequently fail to give a positive result even when fluorides were known to be present. This led to a somewhat detailed study of the conditions during the precipitation and the etching in order to see if in any part of the procedure a lack of strict adherence to minor detail was the reason why a successful test could not be obtained. Without giving a minute description of the numerous experiments, it may be said that considerable variations in the manner of carrying out the precipitation made no apparent difference in the result. The precipitate settles better and slightly more uniform results are obtained when the precipitation is made slowly and at the boiling temperature, although good results have been obtained repeatedly by adding the reagents in the cold and then heating to boiling. The experiments showed, however, that one factor is extremely important—essential in fact,—namely, the temperature during the etching. This one factor was found sufficient to explain the failures experienced, a difference of  $15^{\circ}$  or  $20^{\circ}$  in temperature being enough to prevent the obtaining of a test with a given amount of fluoride.

The differing results obtained at varying temperatures led to an attempt to base an approximately quantitative method on the temperature factor, since something more than a qualitative test is necessary to distinguish between natural and added fluorides. Traces of fluorine are widely distributed in food products and the mere fact that an etching can be obtained is not evidence that fluorides have been added as a preservative. It is essential to know approximately the proportion of fluoride present and the temperature-effect seemed to offer a simple means of determining this. The usual methods for determining fluorine in minerals are, of course, not applicable to the minute quantities that have to be considered here. The objection of lack of delicacy applies also to the various methods based on the loss in weight sustained by





glass of known composition when subjected to the action of hydrofluoric acid. A comparison of the etchings obtained in different tests as regards their apparent intensity has not proven satisfactory in our experience and the same has been found true by others<sup>1</sup>. In order to render such comparisons reliable the etchings must be made by the use of special apparatus to maintain exact conditions, whereas in a test of this kind, if it is to be available for use in general analytical practice, simplicity of apparatus is an important consideration.

With this idea in view, a series of experiments have been carried out on known fluoride solutions in order to determine the temperature corresponding to a definite amount of fluorine. In all cases the fluorine has been precipitated from 150 cc. of solution by means of barium acetate and potassium sulphate, as described above. In fact, up to the point of making the etching test, the procedure is exactly the same as in making a qualitative test.

The apparatus used for heating the crucible during the etching was a simple form of air-bath consisting of a large nickel or iron crucible provided with an asbestos cover in which two platinum crucibles are inserted at equal distances from the center. These two crucibles should be similar in size and shape. One crucible, as shown in the figure, is provided with a waxed plate and condenser, the other with an asbestos lid through which projects a thermometer reaching to the bottom. This control crucible contains 2-3 cc. of concentrated sulphuric acid. The heat is furnished by a burner centrally placed beneath the large crucible. After the apparatus is once adjusted and in working order it should be kept intact and undisturbed. The platinum crucibles should always occupy the same positions and it is necessary to determine, by means of two thermometers whose relative values are known, what temperature on the control thermometer corresponds to the desired temperature in the "etching crucible." This should be done for each of the "etching temperatures" stated below.

It will be realized that an apparatus so simple has its limitations, and in the work which has been done it has not been attempted to control the temperature closer than 5° on either side of the desired point.

As the result of numerous tests, the following temperatures

<sup>1</sup> Ost: Ber. 26, 152.

have been fixed, the corresponding amounts of fluorine being stated in each case.

Temperature.	Distinguishes between.
79°-82°	1 : 25,000 and 1 : 100,000.
113°	1 : 100,000 and 1 : 1,000,000.
136°	1 : 1,000,000 and 1 : 5,000,000.
173°-178°	1 : 5,000,000 and 1 : 25,000,000.
213°-218°	1 : 25,000,000 or less.

This statement means that by running the test for an hour at 136° (131-141°), for example, a distinct etching will be obtained with one part of fluorine in 1,000,000; no test whatever will be given by a dilution of 1 : 5,000,000. Each of these temperature points has been fixed as the result of numerous tests with the apparatus described and they are believed to be definite. It is probable that by more closely regulating the temperature during the etching, the results could be made more nearly quantitative, but it was felt undesirable to attempt this at present on account of the necessary complication of apparatus.

In making a test on a solution containing an unknown amount of fluorine the precipitation is made in the usual manner and the etching carried on for an hour at the lowest temperature (79-82°), counting from the time when the corresponding temperature is reached in the control crucible. At the end of the hour the plate is removed the crucible taken in the tongs, its upper edge gently warmed, and a fresh plate applied. If upon examining the plate just removed no etching is apparent, the test is continued for an hour at the next higher "etching temperature," and so on until a test is obtained or the absence of fluorides is shown. This has been done with a number of unknown solutions with very satisfactory results.

If it can be shown as a result of the examination of pure samples that the fluorine present naturally in a given food material is not above a certain maximum amount, then for the purpose of indicating the presence of added fluorides the test could be materially shortened, it being necessary to make the test at only one temperature. It is hoped to continue the investigation along this line in the future and to examine numerous samples of food and raw products with a view to determining the limiting values for their fluorine content.

In conclusion, it gives us much pleasure to record our indebted-

ness to Mrs. L. C. Krueger, to whom the credit for the analytical work is largely due.

MASS. INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.

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## DETERMINATION OF URANIUM AND VANADIUM.

BY A. N. FINN.

Received July 30, 1906.

A STUDY of the ore carnotite, which is a potassium uranyl vanadate, repeatedly required the determination of uranium and vanadium. This led to a comparison of the various titration methods that have been suggested.

Bělohoubek<sup>1</sup> refers to the reduction of uranium in solution by zinc and sulphuric acid and titration with potassium permanganate. Sutton, in the sixth edition of his "Volumetric Analysis," states that this method is very accurate if care is taken to insure complete reduction which requires from one-quarter to one-half an hour.

Determinations of uranium by this method in solutions of uranyl sulphate gave very satisfactory results provided the potassium permanganate solution was not more than twentieth-normal. When, however, uranium is to be determined from a complex mixture or an ore, great difficulty is found in securing the uranium in a form sufficiently pure for the titration. This is especially true in the presence of vanadium.

The general method of separating the uranium and vanadium from each other and from the various other elements in the ore, is to treat an acid solution of the ore with an excess of sodium carbonate, which precipitates the iron, aluminum, etc., and filter. The filtrate containing the uranium and vanadium is acidified, the carbon dioxide expelled by boiling and the solution is made alkaline with sodium, potassium or ammonium hydroxide. This precipitates the uranium as the corresponding uranate, while the vanadium remains in solution. The uranate is dissolved in sulphuric acid, reduced with zinc and titrated with permanganate. The solution of vanadium is acidified, reduced with sulphur dioxide and titrated with permanganate.

The precipitated uranate is gelatinous and it was found impossible to wash this precipitate free from vanadium, and since

<sup>1</sup> J. pr. Chem. 99, 231.



the uranate is slightly soluble it is not desirable to wash or re-dissolve it many times.

In view of this fact, it became necessary to find an accurate and, if possible, a quicker method for the separation and determination of uranium and vanadium.

This was accomplished by precipitating the uranium in alkaline solution as a phosphate. This precipitate, ammonium uranyl phosphate, is not gelatinous, is insoluble and may easily be washed free from vanadium.

To show that the volumetric method of titrating the reduced solutions with permanganate is consistent in itself, samples of uranium salts containing no vanadium were used and the following results were obtained:

Sample.	Grams.	Per cent. $U_3O_8$ .
Solution No. I .....	9.5058	3.195
	5.1820	3.120
	5.0603	3.167
	5.1570	3.135
Solution No. II .....	10.2941	5.084
	10.2839	5.056
Solution No. III .....	11.7228	5.228
	4.4641	5.276

Samples of solution No. III precipitated with ammonia, ignited and weighed as  $U_3O_8$ , gave the following results:

Grams.	Per cent $U_3O_8$ .
3.81955	5.237
5.3409	5.297

For vanadium, material free from uranium was used and the following results were obtained:

Sample.	Grams.	Per cent. $V_2O_5$ .
Solution No. IV .....	10.7412	0.945
	10.4142	0.946
	11.3310	0.941
	11.4935	0.947
Solution No. V .....	12.8359	1.338
	12.6929	1.340
	15.2051	1.349
	14.1954	1.339
Sample No. VI .....	0.3311	39.127
	0.4341	39.170
	0.3004	39.200

The method suggested for determining uranium and vanadium is, in detail, as follows:

Dissolve a sample of ore that does not contain more than 0.25 gram of  $U_3O_8$  in sulphuric acid (1:5) and evaporate to fumes of the acid. Cool, dilute, add an excess of sodium carbonate and boil until the precipitate settles well. Filter and wash with hot water. Dissolve the precipitate in the smallest possible amount of sulphuric acid, dilute, add an excess of sodium carbonate, boil, filter and wash. Acidify the combined filtrates and wash-waters with sulphuric acid. Add ammonium phosphate (0.5 gram is usually sufficient), heat to boiling and make alkaline with ammonia, boil for a few minutes, filter and wash with hot water containing a little ammonium sulphate, which prevents the finely divided particles of the precipitate from passing through the paper.

The filtrates now contains the vanadium and the precipitate the uranium. Acidify the filtrate with sulphuric acid, pass sulphur dioxide into it until it becomes blue, boil to expel the excess of sulphur dioxide and titrate while hot with permanganate. The iron factor of the permanganate solution multiplied by 1.631 gives the  $V_2O_5$  factor or by 0.9159 gives the vanadium factor.

Dissolve the ammonium uranyl phosphate in sulphuric acid, add some granulated zinc and let the action continue vigorously for at least thirty minutes. Remove the undissolved zinc by filtering over asbestos, using a suction pump, and titrate at about 60° with permanganate (twentieth-normal).

The iron factor of the permanganate solution multiplied by 2.5167 gives the  $U_3O_8$  factor or by 2.133 gives the uranium factor.

By this method of separation, reducing the solutions and titrating with permanganate, the following results were obtained:

Sample.	Grams.	Per cent. $U_3O_8$ .	Per cent. $V_2O_5$ .
Solution No. VII.....	10.7904	1.074	1.429
	21.5602	1.068	....
	15.0921	1.085	1.407
	10.6119	1.063	1.415
<hr/>			
Ore-carnotite I.....	1.0002	11.793	6.363
	1.0013	.....	6.300
	1.0004	11.885	6.261

Sample.	Grams.	Per cent. $U_3O_8$ .	Per cent. $V_2O_5$ .
Ore-carnotite II.....	1.0009	6.755	6.849
	2.0005	6.702	6.526
Ore-carnotite III.....	1.0006	4.873	5.128
	1.0003	4.945	5.358
Ore-carnotite IV.....	1.00045	1.834	....
	1.00025	1.728	....
Ore carnotite V.....	0.9994	0.4094	....
	1.2004	0.4205	....

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## THE SOLUBILITY OF SILVER CHLORIDE IN HYDROCHLORIC ACID AND IN SODIUM CHLORIDE SOLUTIONS.

BY WILLIAM EDWARD BARLOW.

Received August 17, 1906.

It HAS been shown by Dudley<sup>1</sup> that when sodium dioxide is fused in a silver crucible the metal is rapidly attacked, with the formation of a complex oxide.

In 1902 I observed, in ignorance of Dudley's paper, the same action, and showed<sup>2</sup> that when the melt is evaporated or heated with hydrochloric acid (as in the method of determining sulphur by means of fusion with sodium dioxide) the altered silver is converted into chloride, which dissolves (in amounts varying with the temperature and concentration) in the concentrated salt solution present. If the solution is then filtered, and allowed to stand, the greater part—but not the whole—of the silver chloride deposits on cooling. The barium sulphate precipitates from such determinations are almost certain to contain silver. When the solution is filtered hot, and barium chloride solution added before cooling, as in the ordinary sodium peroxide process for determining sulphur, the amount of silver in the barium sulphate may be considerable. In one case 0.03 gram silver chloride was extracted from such a precipitate. This would have occasioned an error of 0.2 per cent. in the sulphur content.

To ascertain the extent to which the reactions above mentioned go on under the conditions of a sodium peroxide fusion the following experiments were made:

<sup>1</sup> Am. Ch. J. 28, 62 (1902).

<sup>2</sup> Inaugural Dissertation, Göttingen, June, 1903.

(a) 22.5 grams of sodium chloride, an amount corresponding to the 15 grams of sodium peroxide used in a fusion, were dissolved in 200 cc. of boiling water, and silver nitrate solution was added to the hot solution until a permanent precipitate was produced. The liquid was then quickly filtered clear, and the dissolved silver was precipitated with hydrogen sulphide. The weight of silver sulphide found corresponded to 0.03 gram silver chloride.

(b) The above experiment was repeated, using, however, 400 cc. of water. The silver chloride dissolved was 0.027 gram. Two or three drops of the silver nitrate solution gave a permanent precipitate in the cold solution. A little of this cold solution, filtered perfectly clear, gave a brown coloration with hydrogen sulphide, showing that small amounts of silver chloride dissolve in such solutions even in the cold.

(c) Twenty-three grams of sodium chloride in 400 cc. of cold water, with about 8 cc. of concentrated hydrochloric acid, dissolved 0.01 gram silver chloride in the cold.

Attempts were then made to estimate volumetrically the amounts of silver chloride taken up by various solutions of sodium chloride and hydrochloric acid. Silver nitrate solution (of known silver content) was added from a burette to the solution to be tested, until, with moderate stirring, a faint white cloud of silver chloride remained. The burette was read, the salt solution brought to 50°, and the addition of silver nitrate continued until a permanent precipitate was again produced. The titration was then made at about 90° in the same solution.

The results of these titrations are tabulated below. In every case the same amount of sodium chloride was used, 23 grams, corresponding to the 15 grams of sodium peroxide used in a fusion. When acid was used it was present in the proportion of 10 cc. of the concentrated acid to 290 cc. of solution. The solutions marked with asterisks were of approximately the same concentration as the filtrate from a peroxide fusion as regards sodium chloride, although they contained somewhat larger amounts of acid.

The results from 100 cc. in Series A and C are probably rendered low by the dilution of the solution with the 15 or 16 cc. of silver nitrate solution. In all other cases the dilution is small enough to have a negligible effect under the conditions described.

The silver nitrate solution contained 0.01485 gram of the salt

per cubic centimeter, corresponding to 0.012525 gram silver chloride per cubic centimeter.

Volume of solution, cc.      20°. cc. of  $\text{AgNO}_3$  solution needed.      50°. cc of  $\text{AgNO}_3$  solution needed.      About 90°. cc of  $\text{AgNO}_3$  solution needed.      Corresponding weight of  $\text{AgCl}$ .

Series A.—23 grams of sodium chloride alone.

100	2.50	7.10	15.70	0.1966
150	1.15	2.30	9.80	0.1227
200	0.50	2.00	7.60	0.0952
300*	0.30	1.40	5.95	0.0745
400*	0.15	1.10	4.55	0.0569
500*	0.10	1.00	4.20	0.0526
700	0.10	0.90	3.90	0.0488

Series B.—10 cc. of conc HCl in each 300 cc. solution.

100	0.05	0.12	0.35	0.0043
150	...	0.18	0.70	0.0086
200	0.10	0.25	0.90	0.0112
300*	...	0.35	1.35	0.0169
400*	0.20	0.50	1.90	0.0238
500*	...	0.60	2.20	0.0275
700	0.20	0.75	3.20	0.0400

Series C.—Sodium chloride and HCl together.

100	2.20	5.70	16.00	0.2004
150	1.50	3.80	10.50	0.1315
200	0.80	2.90	9.30	0.1165
300*	0.40	2.10	7.50	0.0939
400*	0.35	1.50	6.70	0.0839
500*	0.35	1.80	6.80	0.0852
700	0.45	2.00	7.70	0.0964

In the following table the sums of the results of Series A and B, at 90°, are placed side by side with the corresponding results of C.

Volume of solution, cc.	Sums of results of A and B, cc.	Results of Series C, cc.
100	16.05	16.00
150	10.50	10.50
200	8.50	9.30
300	7.30	7.50
400	6.45	6.70
500	6.40	6.80
700	7.10	7.70

The figures show that the solubility of silver chloride in solutions of sodium chloride falls off (at a gradually diminishing rate) with diminishing concentration, and that the amounts of silver chloride dissolved in the acid are directly proportional to the volumes of acid (of fixed concentration) used. The increase in

solubility near the end of Series C is due to the larger amounts of acid present. The results of C correspond nearly enough with the sums of A and B to show that the effects of the sodium chloride and acid are independent. These facts become even more evident when the results are expressed in the form of curves.

It is clear that the use of a silver dish for sulphur determinations by fusion with sodium dioxide introduces complications. The removal of the dissolved silver is best effected by precipitation with perfectly pure hydrogen sulphide. Dilution to 400 cc., and filtering after cooling, does not suffice to remove all the silver. Dilution to a much larger volume would involve either a tedious evaporation over the alcohol lamp before precipitation with barium chloride or a considerable error owing to the solubility of barium sulphate in the large volume of solution. It is simpler and more satisfactory to avoid the difficulty by using a nickel crucible or dish.

METALLURGICAL LABORATORY,  
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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 124.]

**RESEARCHES ON QUINAZOLINES (SIXTEENTH PAPER).  
SYNTHESIS OF 6-NITRO-2-METHYL-4-KETODIHY-  
DROQUINAZOLINES FROM 5-NITROACET-  
ANTHRANIL AND PRIMARY AMINES.<sup>1</sup>**

BY MARSTON TAYLOR BOGERT AND ELLEN PARMELEE COOK.

Received July 13, 1906

In previous papers<sup>2</sup> we have reported upon 5- and 7-nitro-4-ketodihydroquinazolines. The following article contains a record of some experiments in the synthesis of derivatives of the 6-nitro isomer.

Dehoff,<sup>3</sup> by the direct nitration of 2-methyl-4-ketodihydroquinazoline, obtained a nitro derivative in which the position of the nitro group remained unknown until Thieme<sup>4</sup> prepared the same substance by heating the ethyl ester of 5-nitro-2-acetamino-

<sup>1</sup> Read at the meeting of the New York Section of the American Chemical Society, May 11, 1906.

<sup>2</sup> Bogert and Chambers: *This Journal*, 27, 649 (1905); Bogert and Seil: *Ibid.* 27, 1305 (1905); 28, 884 (1906); Bogert and Steiner: *Ibid.* 27, 1327 (1905).

<sup>3</sup> *J. pr. Chem.* [2] 42, 347 (1890).

<sup>4</sup> *Ibid.* [2] 43, 473 (1891).



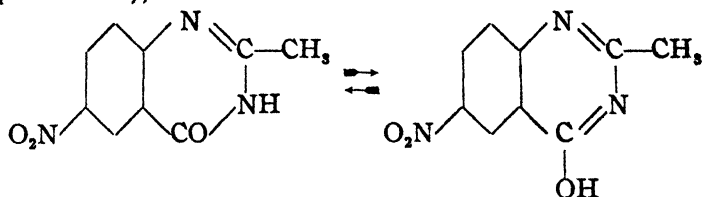
5-Nitro-2-toluidine was acetylated in the usual way, and the acetyl derivative crystallized from alcohol, when it showed a melting-point of  $198^{\circ}$ . This acetyl derivative was then oxidized by potassium permanganate in presence of magnesium sulphate. The 5-nitroacetanthranilic acid thus obtained melted after several recrystallizations at  $221.5^{\circ}$  (corr.). This agrees with the melting-point ( $221^{\circ}$ ) given by Ullmann,<sup>1</sup> but not with that reported by Seidel ( $213^{\circ}$ ).<sup>2</sup> The yield was about 65 per cent.

The nitroacetanthranilic acid was heated for five minutes with acetic anhydride, and the solution then allowed to cool. Long, colorless needles crystallized out, melting at  $161-162^{\circ}$  (corr.). The excess of acetic anhydride was removed by washing with dry ether or with carbon tetrachloride.

Calculated for  $C_9H_6O_4N_2$ : C, 52.42; H, 2.91. Found: C, 52.24 and 52.14; H, 2.92 and 2.76.

Like the other nitroacetanthranils, this hydrolyzes slowly in moist air, or rapidly when boiled with water, yielding the nitroacetanthranilic acid again.

*6-Nitro-2-Methyl-4-Ketodihydroquinazoline (6-Nitro-2-Methyl-4-Oxyquinazoline),*



5-Nitroacetanthranil was heated with dilute aqueous ammonia, the mixture then warmed with dilute potassium hydroxide solution to change any intermediate amide to quinazoline, and a current of carbon dioxide passed through the solution. The quinazoline precipitated as an amorphous powder, which was crystallized from hot alcohol.

The same product was obtained by dissolving the nitroacetanthranilic acid in an excess of dilute ammonium hydroxide solution, evaporating to dryness, and heating the residue at  $125^{\circ}$  in an oil-bath. The yield by this method was very poor.

As already stated, this body was first prepared by Dehoff, and later by Thieme. The properties of the substance prepared by

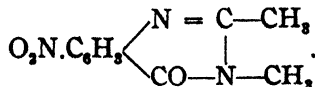
<sup>1</sup> Ber. 36, 1801 (1903).

<sup>2</sup> Chem. Centr. 1902, II, 554.



ns agree entirely with those of the compound obtained by Dehoff and Thieme, both in solubilities and melting-point. They both found that their product darkened between  $230^{\circ}$  and  $280^{\circ}$ , while ours begins to darken at about  $266^{\circ}$ , and melts at  $278-281^{\circ}$  (corr.).

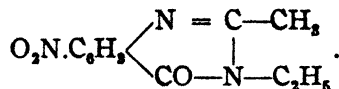
*6-Nitro-2,3-Dimethyl-4-Ketodihydroquinazoline,*



5-Nitroacetantranil was warmed for a few minutes with methylamine, and the product recrystallized from alcohol. It then melted at  $164-165^{\circ}$  (corr.), and was insoluble in alkalis.

Dehoff<sup>1</sup> prepared this substance by heating the potassium salt of the 2-methyl compound with methyl iodide at  $120^{\circ}$ , and also by the action of fuming nitric acid (sp. gr. 1.5) upon 2,3-dimethyl-4-ketodihydroquinazoline, while Thieme made it from the corresponding silver salt and methyl iodide, and also by heating nitroacetantranilic acid ethyl ester with methylamine for several hours at  $130^{\circ}$ . Both authors give the melting-point as  $165^{\circ}$ .

*6-Nitro-2-Methyl-3-Ethyl-4-Ketodihydroquinazoline,*

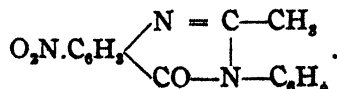


This was prepared in similar fashion from 5-nitroacetantranil and ethylamine. It crystallizes from alcohol in needles which melt at  $166^{\circ}$  (corr.).

Calculated for  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}_3$ : N, 18.02. Found: N, 18.07 and 17.95.

The same compound was obtained when the sodium salt of the nitromethylquinazoline was treated with ethyl iodide.

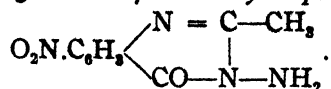
*6-Nitro-2-Methyl-3-Phenyl-4-Ketodihydroquinazoline,*



This was made by heating the nitroacetantranil with aniline. It is difficultly soluble in alcohol, and crystallizes from glacial acetic acid in small, compact, light-yellow crystals, which melt at  $219-220^{\circ}$  (corr.).

Calculated for  $\text{C}_{18}\text{H}_{11}\text{O}_3\text{N}_3$ : N, 14.95. Found: N, 14.80.

<sup>1</sup> Loc. cit.

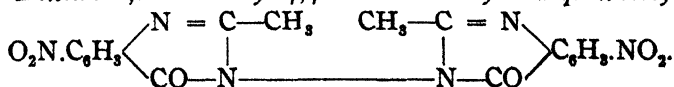
*6-Nitro-2-Methyl-3-Amino-4-Ketodihydroquinazoline,*

When the nitroacetanthranil was heated with a 50 per cent. aqueous solution of hydrazine hydrate, there resulted a deep-red solid, soluble in hot water. Colorless needles crystallized from the aqueous solution on cooling, which melted at 208–209° (corr.).

Calculated for  $\text{C}_9\text{H}_8\text{O}_3\text{N}_4$ : C, 49.09; H, 3.64; N, 25.45. Found: C, 49.00; H, 3.81; N, 25.56.

The compound is readily soluble in dilute alcohol, from which it crystallizes in long, colorless needles. It dissolves in solutions of the caustic alkalis with a deep red color.

When it was crystallized from glacial acetic acid and the crystals allowed to dry in the air, the compound showed a nitrogen content of 23.31 per cent. When this air-dried material was heated at 135° until the weight became constant, it lost 9.27 per cent. of acetic acid. This would make the nitrogen percentage in the substance dried at 135°, 25.68 per cent. On analysis, it was found to be 25.65 per cent. This appears to indicate the presence of acetic acid of crystallization in the proportion of two molecules of the acid to five of the quinazoline. This may not, however, represent the actual proportion between acid and quinazoline in the crystals as they first separate, as it is not unlikely that the crystals analyzed had already lost some of their acetic acid on standing in the air.

*6,6'-Dinitro-2,2'-Dimethyl-4,4'-Diketotetrahydrodiquinazolyl,*

One molecule of hydrazine (using a 50 per cent. aqueous solution of the hydrate) was added to two of the nitroacetanthranil, and the mixture heated for twenty minutes at 160–180° in an oil-bath. The cooled melt was pulverized and heated with alcohol, to remove aminoquinazoline, unchanged anthranil, and other impurities. The residual diquinazolyl was crystallized from glacial acetic acid. Small, compact crystals resulted, which melted with darkening at 281–286° (corr.). The yield was very poor.

Calculated for  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_4$ : N, 20.59. Found: N, 17.71 and 18.00.

These analytical results made it quite clear that we did not have the free diquinazolyl in hand. The air-dried substance was, therefore, dried to constant weight at 145°. In this drying at 145° it lost 12.1 per cent. of acetic acid, which would make the nitrogen percentage in the acetic acid-free substance, 20.3. The crystals analyzed apparently contained one molecule of the diquinazolyl to one of acetic acid.

Calculated for  $C_{18}H_{12}O_6N_6 \cdot CH_3COOH$ : N, 17.95.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,  
July, 1906

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

## RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(SIXTH PAPER.)

BY TREAT B. JOHNSON.

Received July 19, 1906

THE object of the work<sup>1</sup> described in this paper was to prepare some new thiol acids, I, and examine their behavior towards thiocyanates, II, and isothiocyanates, III.

R.COSH,  
I.

R.SCN,  
II.

R.NCS.  
III.

It has been shown in several papers from this laboratory<sup>2</sup> that thiocyanates and isothiocyanates can be sharply distinguished by their behavior towards thiol acids, I. Thiocyanates, II, react with thiol acids in two ways. The most commonly observed reaction is a direct addition to the acid to give a dithiourethane, IV. Certain ones, on the other hand, react in a complicated manner to give thiol esters, V, and thiocyanic acid, VI.



IV.



VI.

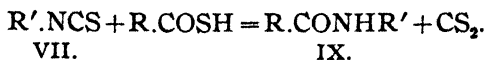
V.

Alkyl isothiocyanates, VII, and acyl isothiocyanates, VIII, react

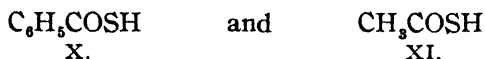
<sup>1</sup> All the experimental work described in this paper was accomplished by advanced Senior students (1906), who had completed the required laboratory course in practical organic chemistry.—T. B. JOHNSON.

<sup>2</sup> Wheeler and Merriam: This Journal, 23, 283; 24, 439; Wheeler and Johnson: Ibid. 24, 680; 26, 185; Wheeler and Jamieson: Ibid. 24, 744.

in an entirely different manner with thiol acids to form substituted acid amides, IX, and carbon bisulphide as follows:

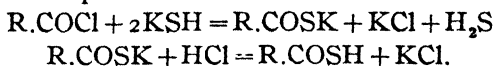


The above reactions have hitherto been applied with only two thiol acids, *viz.*, thiolbenzoic, X, and thioacetic acids, XI. It seemed of interest to the writer to decide whether other thiol



acids might be used to distinguish between thiocyanates and isothiocyanates. Furthermore, we wished to determine whether the tendency for a thiocyanate to give a dithiourethane, IV, or a thiol ester, V, might be influenced by the negative character of the thiol acid.

We describe in this paper four new thiol acids, *viz.*, phenylthioacetic,  $\text{C}_6\text{H}_5\text{CH}_2\text{COSH}$ , meta- and parabromthiobenzoic,  $\text{Br.C}_6\text{H}_4\text{COSH}$ , and metanitrothiobenzoic,  $\text{NO}_2\text{C}_6\text{H}_4\text{COSH}$ , acids. They were prepared by dissolving the corresponding acid chlorides in an aqueous or alcoholic solution of potassium hydrosulphide and then treating the resulting potassium salts with hydrochloric or sulphuric acids.



Meta- and parabromthiobenzoic acids and metanitrothiobenzoic acid are of especial interest as the first members of this class of thiol acids that have been obtained as solids at ordinary temperature. They were very stable and could be kept for several weeks without change in a dry atmosphere. Phenylthioacetic acid was obtained as an oil.

Carius<sup>1</sup> has described a solid thiosalicylic acid,  $\text{OH.C}_6\text{H}_4\text{COSH}$ . He prepared it by acting on salicylic acid with phosphorus pentachloride and then treating the acid chloride with barium hydrosulphide. It does not seem probable that Carius was dealing with this thiol acid, since Anschütz and his co-workers<sup>2</sup> have shown that phosphorus halides do not react with salicylic acid to give the acid chloride,  $\text{HO.C}_6\text{H}_4\text{COCl}$ . The first oxy-acid chloride

<sup>1</sup> Ann. 129, 11.

<sup>2</sup> Ibid. 228, 308; 239, 316, 333; 239, 304.

isolated was 3,5-dichlorsalicyl chloride,  $\text{Cl}_2(\text{HO})\cdot\text{C}_6\text{H}_2\text{COCl}$ .<sup>1</sup> Anschütz and his students have recently described a large number of aromatic oxy-acid chlorides.<sup>2</sup>

We examined the behavior of the above thiol acids towards methyl, ethyl and benzyl thiocyanate. They reacted with these thiocyanates to give the corresponding dithiourethanes. The reactions were very smooth and we did not detect any evidence of the formation of thiol esters. So far as we were able to judge, the four acids did not show any appreciable difference in their tendency to combine with thiocyanates.

Our thiol acids reacted normally with an isothiocyanate. Phenylthioacetic, parabromthiobenzoic and metanitrothiobenzoic acids reacted quantitatively with phenyl isothiocyanate to give the corresponding acid anilides.

Phenylacetanilide,  $\text{C}_6\text{H}_5\text{CH}_2\text{CONHC}_6\text{H}_5$ .<sup>3</sup>

Parabrombenzoylanilide,  $\text{Br}\cdot\text{C}_6\text{H}_4\text{CONHC}_6\text{H}_5$ .<sup>4</sup>

Metanitrobenzoylanilide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{CONHC}_6\text{H}_5$ .<sup>5</sup>

COMPARATIVE BOILING- AND MELTING-POINTS OF THE THIOL ACIDS USED IN OUR THIOCYANATE RESEARCHES, AND THE BOILING- AND MELTING-POINTS OF THEIR CORRESPONDING ACID CHLORIDES.

Acid Chloride	B P	M. P
Acetyl chloride, $\text{CH}_3\text{COCl}$ .....	55°	..
Phenylacetyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{COCl}$ .....	102° at 17 mm.	..
Benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$ .....	198°	..
Metabrombenzoyl chloride, $\text{Br}\cdot\text{C}_6\text{H}_4\text{COCl}$ ...	243°	..
Parabrombenzoyl chloride, $\text{Br}\cdot\text{C}_6\text{H}_4\text{COCl}$ ...	.	41°
Metanitrobenzoyl chloride, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{COCl}$ ....	..	35°
Thiol Acid.		
Thioacetic acid, $\text{CH}_3\text{COSH}$ .....	93°	.
Phenylthioacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{COSH}$ .....	..	..
Thiobenzoic acid, $\text{C}_6\text{H}_5\text{COSH}$ .....	..	24°
Metabromthiobenzoic acid, $\text{Br}\cdot\text{C}_6\text{H}_4\text{COSH}$ .....	..	58°
Parabromthiobenzoic acid, $\text{Br}\cdot\text{C}_6\text{H}_4\text{COSH}$ .....	..	78-79°
Metanitrothiobenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{COSH}$ .....	..	89-90°

<sup>1</sup> Anschütz: Ann. 346, 300; Ber. 30, 221.

<sup>2</sup> Ann. 346, 286-360.

<sup>3</sup> Hofmann: Ber. 13, 1225.

<sup>4</sup> Reyeill: Ann. 222, 178.

<sup>5</sup> Schotten: Ber. 21, 2245.

## EXPERIMENTAL PART.

BY ERNEST BATEMAN, ERIK SCHJÖTH PALMER AND CHARLES ANDREW BRAUTLECHT.

*Phenylthioacetic Acid*,  $C_6H_5CH_2COSH$ .—This acid was obtained in the form of its potassium salt when phenylacetyl chloride was warmed on the steam-bath with an aqueous solution of potassium hydrosulphide. After the acid chloride had completely dissolved the solution was acidified with sulphuric acid. The thiol acid separated as a limpid oil. It did not solidify after standing for several weeks. When exposed to the atmosphere it was slowly oxidized to the disulphide.

*Diphenylacetyl Disulphide*  $(C_6H_5CH_2COS)_2$ .—This compound was prepared by suspending finely pulverized iodine in an aqueous solution of the sodium salt of phenylthioacetic acid. The sulphide separated as a crystalline deposit. It was purified for analysis by recrystallization from 95 per cent. alcohol. It deposited in transparent plates that melted at  $62^\circ$ . It was insoluble in sodium hydroxide solution. Carbon and hydrogen determinations gave: C, 63.73; H, 5.0; calculated for  $C_{18}H_{14}O_2S_2$ , C, 63.57; H, 4.63.

*Action of Phenylthioacetic Acid on Phenyl Isothiocyanate*.—Molecular proportions<sup>1</sup> of phenylthioacetic acid and phenyl isothiocyanate were heated together at  $100^\circ$ . Carbon bisulphide was evolved and we obtained a crystalline substance. It deposited from 95 per cent. alcohol in prisms that melted at  $117-118^\circ$ . It was identified as phenylacetanilide.<sup>1</sup> It did not contain sulphur and when mixed with phenylacetanilide the melting point was not lowered.

*Phenylacetyldithiomethylcarbamate*,  $C_6H_5CH_2CO.NH.CSSCH_3$ .—Molecular proportions of phenylthioacetic acid and methyl thiocyanate were heated together in a boiling water-bath for about one hour. We obtained a thick oil that solidified on cooling. The compound crystallized from alcohol in slender prisms that melted at  $133^\circ$  to an oil. They were dissolved by sodium hydroxide and were reprecipitated from the alkaline solution by acids. The analysis (Kjeldahl) gave: N, 6.24; calculated for  $C_{10}H_{11}ONS_2$ , 6.22.

*Phenylacetyldithioethylcarbamate*,  $C_6H_5CH_2CO.NH.CSSC_2H_5$ .—This compound was obtained when a mixture of molecular proportions of phenylthioacetic acid and ethyl thiocyanate was heated

<sup>1</sup> Hoffman: Loc. cit.

at 100° for three hours. It deposited from alcohol in lemon-yellow prisms that melted at 125° to an oil. The analysis (Kjeldahl) gave, N, 5.74; calculated for  $C_{11}H_{13}ONS_2$ , 5.85.

*Phenylacetyldithiobenzylcarbamate*,  $C_6H_5CH_2CO.NH.CSSCH_2C_6H_5$ .—From phenylthioacetic acid and benzyl thiocyanate. It was purified for analysis by recrystallization from alcohol. It deposited in lemon-yellow prisms that melted at 123°. The analysis gave: N, 4.68; calculated for  $C_{16}H_{15}ONS_2$ , 4.65.

*Metabromthiobenzoic Acid*,  $Br.C_6H_4.COSH$ .—Metabrombenzoyl chloride<sup>1</sup> did not react readily with potassium hydrosulphide in aqueous solution. In order to obtain a complete reaction it was necessary to heat them at 100° for several hours. When the alkaline solution was acidified with hydrochloric acid the thiol acid separated as an oil. This oil was extracted with ether and the solution dried over calcium chloride. When the ether was removed by distillation we obtained the thiol acid as an oil which finally solidified. It was crystallized from petroleum ether and deposited as a light yellow, crystalline powder that melted at 58°. The acid was very soluble in alcohol, ether and benzene. The analysis gave: Br, 36.35. Calculated for  $C_7H_5OBrS$ , 36.85.

*Metabrombenzoyldithiomethylcarbamate*,  $Br.C_6H_4.CONHCSSCH_3$ .—This compound was prepared by heating a mixture of metabromthiobenzoic acid and methyl thiocyanate in a boiling water-bath for a few minutes. It deposited from 95 per cent. alcohol in distorted needles that melted at 124°. The analysis gave: N, 5.1; calculated for  $C_9H_8ONBrS_2$ , 4.83.

*Metabrombenzoyldithioethylcarbamate*,  $Br.C_6H_4.CO.NHCSSC_2H_5$ .—From metabromthiobenzoic acid and ethyl thiocyanate. It deposited from alcohol in needle-like prisms that melted at 131°. The analysis gave: N, 4.3; calculated for  $C_{10}H_{10}ONBrS_2$ , 4.60.

*Metabrombenzoyldithiobenzylcarbamate*,  $Br.C_6H_4.CONHCSSCH_2C_6H_5$ .—From benzyl thiocyanate and metabromthiobenzoic acid. It deposited from 95 per cent. alcohol in prismatic crystals. They melted at 113°. The analysis gave: N, 4.0; calculated for  $C_{15}H_{12}ONBrS_2$ , 3.82.

*Parabromthiobenzoic Acid*,<sup>2</sup>  $Br.C_6H_4.COSH$ .—When parabrom-

<sup>1</sup> Sudborough: J. Chem. Soc. 67, 590.

<sup>2</sup> This acid was first prepared by Dr. G. S. Jamieson in 1903.

benzoyl chloride was added to an alcoholic solution of potassium hydrosulphide an immediate reaction took place with separation of potassium chloride. The solution was warmed a few minutes to complete the reaction, then concentrated to a small volume and the insoluble potassium chloride removed by filtration. When the filtrate was cooled we obtained a deposit of yellow prisms. They were very soluble in water and were identified as the potassium salt of parabromthiobenzoic acid. A bromine determination gave: Br, 30.85; calculated for  $C_7H_4OBrSK$ , 31.35.

When this potassium salt was dissolved in cold water and the solution acidified with hydrochloric acid the thiol acid deposited in the form of colorless, flat prisms. It dissolved in hot alcohol and deposited on cooling in prisms that melted at  $78-79^\circ$  to a clear oil. A bromine determination gave: Br, 36.50; calculated for  $C_7H_5OBrS$ , 36.85.

*Action of Parabromthiobenzoic Acid on Phenyl Isothiocyanate.*—When the thiol acid was heated with the isothiocyanate an immediate reaction took place with evolution of carbon bisulphide. We obtained a compound that deposited from alcohol in plates. They melted at  $201-202^\circ$  to a clear oil and did not respond to a test for sulphur. A nitrogen determination (Kjeldahl) agreed with the calculated value in *parabrombenzoylanilide*,<sup>1</sup>  $Br.C_6H_4.CONHC_6H_5$ . Found, 5.3; calculated for  $C_{13}H_{10}ONBr$ , 5.07.

This same anilide<sup>2</sup> melting at  $201-202^\circ$  was also prepared by warming the thiol acid with a molecular proportion of aniline.

*Parabrombenzoyldithiomethylcarbamate*,  $Br.C_6H_4.CO.NHCSSCH_3$ .—From parabromthiobenzoic acid and methyl thiocyanate. It deposited from 95 per cent. alcohol in distorted needles that melted at  $152^\circ$  to a clear oil. The analysis gave: N, 4.80; calculated for  $C_9H_8ONBrS_2$ , 4.82.

*Parabrombenzoyldithioethylcarbamate*,  $Br.C_6H_4.CO.NH.CSSC_2H_5$ .—From ethyl thiocyanate and parabromthiobenzoic acid. It deposited from alcohol in pale yellow needles that melted at  $116^\circ$  to a yellow oil. The analysis gave: N, 4.63; calculated for  $C_{10}H_{10}ONBrS_2$ , 4.60.

*Metanitrothiobenzoic Acid*,  $NO_2.C_6H_4.COSH$ .—This acid was ob-

<sup>1</sup> Loc. cit.

<sup>2</sup> Raveill states that this anilide melts at  $197^\circ$ . Ann. 222, 178.



tained in the form of its potassium salt by adding metanitrobenzoyl chloride to an aqueous or alcoholic solution of potassium hydrosulphide. When an aqueous solution of the salt was acidified with sulphuric or hydrochloric acid the thiol acid separated as an oil which soon solidified. This acid is unstable if moist, and all operations must be performed at low temperatures in order to avoid decomposition. The acid was insoluble in water, but very soluble in acetone, warm alcohol and benzene. It deposited from dilute alcohol in light yellow, prismatic crystals that showed signs of melting at  $85^{\circ}$  and then melted sharply at  $89-90^{\circ}$  to a clear oil. The analysis gave: N, 7.69 and 7.7; calculated for  $C_7H_5O_3NS$ , 7.65.

The sodium salt was very soluble in water. It deposited from 95 per cent. alcohol in irregular prisms. The analysis gave: N, 6.85; calculated for  $C_7H_4O_3NSNa$ , 6.82.

*Action of Metanitrothiobenzoic Acid on Phenyl Isothiocyanate.*—A mixture of molecular proportions of the isothiocyanate and thiol acid was heated in a boiling water-bath for about two hours. Carbon bisulphide was copiously evolved. We obtained a crystalline substance that was difficultly soluble in water. It deposited from alcohol in plates that melted at  $154^{\circ}$  and did not respond to a test for sulphur. A nitrogen determination agreed with the calculated value in *metanitrobenzoylanilide*,<sup>1</sup>  $\overset{3}{NO_2} \cdot C_6H_4 \cdot \overset{1}{CONHC_6H_5}$ . The analysis gave: N, 12.0; calculated for  $C_{12}H_{10}O_3N_2$ , 11.6.

*Metanitrobenzoyldithiomethylcarbamate*,  $\overset{3}{NO_2} \cdot C_6H_4 \cdot \overset{1}{CO} \cdot NH \cdot CSSCH_3$ .—This compound was prepared by heating together molecular proportions of methyl thiocyanate and metanitrothiobenzoic acid. The reaction was very smooth and complete in a few minutes. The urethane was very soluble in benzene and sparingly soluble in alcohol. It deposited from benzene in yellow needles that melted at  $162^{\circ}$ . The analysis gave: N, 10.64; calculated for  $C_8H_5O_3N_2S_2$ , 10.93.

*Metanitrobenzoyldithioethylcarbamate*,  $\overset{3}{NO_2} \cdot C_6H_4 \cdot \overset{1}{CO} \cdot NH \cdot CSSC_2H_5$ .—From ethyl thiocyanate and metanitrothiobenzoic acid. This compound was sparingly soluble in cold alcohol and deposited from hot alcohol in yellow prisms that melted at  $158^{\circ}$  to a

<sup>1</sup> Schotten; Ber. 21, 2245.

clear oil. The analysis gave: N, 10.5; calculated for  $C_{10}H_{16}O_2N_2S_2$ , 10.37.

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## THE CHLOR-HYDROCHLORIDES OF PINENE AND FIRPENE.

BY G. B. FRANKFORTER AND FRANCIS C. FRARY.

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*The Purification of Pinene and Firpene.*—The pinene used in the preparation of the following compounds was obtained from the common white turpentine by distilling with steam, drying and redistilling until the boiling-point was constant at 156–157°. An analysis showed that the substance consisted entirely of hydrogen and carbon, and the physical properties corresponded with those of pure pinene.

The firpene used was obtained from the western fir by distilling the crude pitch with steam. The water-white terpene was dried and redistilled several times. Combustion gave numbers which corresponded with the formula  $C_{10}H_{16}$ . Molecular weight determinations also gave numbers which corresponded well with the above formula. Its odor, its specific gravity, its refractive index and its optical activity differed from the pure pinene. The chemical properties, likewise, differed from pinene. The following is a comparison of the physical properties of the two substances:

	Pinene.	Firpene.
Boiling-point.....	156°–157°	153°–153.5°
Sp. gr. at 20°.....	0.8647	0.8598
Index of refraction at 20°... ..	1.46336	1.47299
Optical activity ( $\alpha$ ) <sub>D</sub> .....	+14.34	–47.2

*Preparation of Pinene Hydrochloride.*—The pinene hydrochloride prepared by the common method contains a considerable quantity of soluble oily and resinous matter from which it is separated with great difficulty. In fact, we were unable to find a satisfactory method for the separation of the hydrochloride from these oily and resinous substances. A new method therefore seemed important. After many trials, the following process was finally chosen as being entirely satisfactory. Pure pinene was mixed with about an equal volume of dry chloroform in a large round-bottomed flask, mixed thoroughly and cooled below 0°. Pure

dry hydrochloric acid gas was passed into the liquid until it became saturated with the acid.

It was necessary to pass the gas into the pinene very slowly at first as considerable heat is generated. After saturation, an equal volume of water was added and the excess of acid removed by the addition of sodium bicarbonate. This mixture was immediately subjected to steam distillation. The chloroform which passed over first contained a considerable quantity of the hydrochloride; the greater part, however, remained in the flask after all the chloroform had been removed. Further steam distillation carried it over into the condenser where it solidified in comparatively pure form. The chloride still contained a very small quantity of a colorless oil. All the resinous matter, however, was completely removed. After most of the hydrochloride had distilled over, the oil began to appear. It is important that the solid chloride should be removed from the condenser before the oil begins to pass over as they readily mix and are difficult to separate from each other. It was found that the hydrochloride could be removed by cooling to  $-30^{\circ}$ , filtering off the crystals and drying between sheets of filter-paper. Two or three crystallizations of the chloride from alcohol gave a substance which melted at  $130-131^{\circ}$ , which is the melting-point of pure pinene hydrochloride as stated by Long.<sup>1</sup> This method has been used in the preparation of all of the hydrochlorides and hydrobromides of both pinene and firpene and of the terpene from the Norway pine.

#### CHLOR-HYDROCHLORIDES OF PINENE AND FIRPENE.

*Pinene Pentachlorhydrochloride*,  $C_{10}H_{11}Cl_5HCl$ .—Several chlorine compounds have been prepared from pinene, the most important of which are nitrosyl-chloride<sup>2</sup> pinene dichlorhydrochloride<sup>3</sup> of questionable composition and trichloride of dipentene.<sup>4</sup> These and a few other compounds have been described but owing to the difficulty experienced in purifying them, only the above-mentioned compounds have been studied. Most of these chlorides were made by difficult complex methods which have been tried by others and found to give a mixture of several compounds with such closely associated properties that separation seems to us

<sup>1</sup> This Journal, 21, 637.

<sup>2</sup> Ibid., 9, 554 (1887).

<sup>3</sup> J. Russ. Chem. Soc. 25, 383.

<sup>4</sup> Ann. 270, 196.

next to impossible. Hypochlorous acid has been mentioned in a number of experiments. This reagent gives impure oxychlor-terpenes which could not be separated. In a single other case, Hesse<sup>1</sup> used chlorine in a carbon disulphide solution. Examination of this method showed that in each case the reaction was deep-seated and several compounds, often of oily nature, were formed, together with sulphur and sulphur compounds.

Many different methods were tried by others without satisfactory results. Hydrochloric acid with potassium permanganate was finally tried and found to give good results. The method adopted was as follows: A known weight of the terpene hydrochloride was dissolved in 5 times its weight of pure chloroform and an equal quantity of water added and stirred. An equal weight of potassium permanganate was added and hydrochloric acid (sp. gr. 1.2) added cautiously. The flask was corked and allowed to stand for some time. Fresh additions of hydrochloric acid and permanganate were added from time to time. The process was continued for a week, taking care to keep an excess of chlorine in the solution. The chloroform was then separated from the water and a few drops of alcohol added to absorb the excess of chlorine. The chloroform solution was of a yellowish green color, due to the presence of free chlorine. After removing the chloroform by evaporation, the solid amorphous residue was crystallized from warm alcohol, dissolved in ether, clarified with bone-black and recrystallized several times from alcohol.

The crystallized substance resembled somewhat the original pinene hydrochloride in belonging to the isometric crystal system. The corrected melting-point, however, was 173-174°.

These crystals were deliquescent in both ether and chloroform vapors. Evaporation of the ether and chloroform left an amorphous substance. The presence of alcohol, however, reproduced the crystals. Analyses of the pure substance gave the following numbers:

0.2250 gram substance gave 0.5619 gram AgCl.

0.2044 gram substance gave 0.2586 gram CO<sub>2</sub> and 0.0562 gram H<sub>2</sub>O.

Calculated for C<sub>10</sub>H<sub>12</sub>Cl<sub>4</sub>: C, 34.74; H, 3.51; Cl, 61.69. Found: I. Cl, 61.75; II. C, 34.50; H, 3.05.

<sup>1</sup> Ann. 270, 196.

An attempt to make the pentachloride directly from pinene instead of the hydrochloride by chlorinating with hydrochloric acid and potassium permanganate, failed. The result in every attempt was a heavy oily mass with distinctly aromatic odor. This oil readily decomposed in the air, changing to a brown mass.

From the fact that this compound can not be prepared without first converting the terpene into the hydrochloride, we have represented it as well as the other analogous chlorine compounds which follow as a hydrochloride.

*Pinene Hexachlorhydrochloride*,  $C_{10}H_{10}Cl_6HCl$ .—Pinene hydrochloride was dissolved in chloroform and treated with dry chlorine in bright sunlight. Chlorine was passed into the solution for eight hours. Upon evaporation a residue was left which resembled somewhat the pentachloride. It was purified by recrystallizing from alcohol several times or until the melting-point became constant at  $218^{\circ}$ . The chlorine determination gave results higher than the theoretical but near enough to indicate that the compound is a hepta compound, 66.51 per cent. of chlorine being found. Calculated for  $C_{10}H_{10}Cl_6HCl$ , 65.43 per cent.

*Pinene Nonachlorhydrochloride*,  $C_{10}H_8Cl_9HCl$ .—In the preparation of pinene hexachlorhydrochloride, there was left in solution after the hexachlor compound had crystallized out of carbon tetrachloride, a sticky substance which refused to crystallize. This substance was dissolved in pure carbon tetrachloride and dry chlorine passed through the solution until it remained a bright yellow color after standing six hours in bright sunlight without the further addition of chlorine. Upon evaporation of the tetrachloride a waxy sticky mass remained, having about the consistency of "grained honey." No further reaction seemed to take place after standing several months. This waxy mass was then extracted with boiling 95 per cent. alcohol, when the oily part dissolved, leaving most of the crystals. By repeated extraction with large quantities of alcohol, the whole mass of crystals dissolved. Upon cooling the alcoholic solution, most of the substance crystallized out again. After recrystallization the substance had a melting-point of  $263\text{--}264^{\circ}$  (uncor.). Further recrystallization failed to change the melting-point.

Analysis of this substance gave the following results:

1. 0.1950 gram substance gave 0.5655 gram AgCl.
2. 0.1910 gram substance gave 0.5579 gram AgCl.
3. 0.1581 gram substance gave 0.3473 gram AgCl.
4. 0.1457 gram substance gave 0.3228 gram AgCl.

Calculated for  $C_{10}H_7Cl_9HCl$ : Cl, 73.47. Found: Cl, 71.69, 72.22, 72.14, 72.76.

It will be seen that the chlorine found is lower than the theoretical. It was at first thought that perhaps the substance was a mixture of nona- and decachlorhydrochloride. The constant melting-point, however, indicated a single substance. Finally, a molecular weight determination was made and the results obtained corresponded closely with the above theory.

The substance resembles the pentachlorhydrochloride in its crystal form and properties but it is much less soluble in alcohol and has less odor. Alcoholic silver nitrate did not remove any of the chlorine, while several months' standing with excess of silver oxide removed only a very small part of the chlorine. Sodium methylate in absolute alcohol seemed to have no effect upon it. Neither boiling nitric acid (sp. gr. 1.4) nor a boiling mixture of this with two parts sulphuric acid had any apparent effect upon it. It is more soluble in absolute alcohol than in 95 per cent. alcohol and is very soluble in benzene, ether, chloroform and carbon tetrachloride.

*The Action of Bromine on the Hydrochloride.*—It was found that bromine would not act readily upon the hydrochloride. The hydrochloride was exposed to the sunlight in the presence of bromine for a month, no change evidently having taken place during that time. By long treatment with hydrobromic acid in the presence of potassium permanganate and sulphuric acid, an aromatic oil was obtained. This oil proved to be a bromide but has not been obtained in pure enough state for analysis.

#### COMPOUNDS OF FIRPENE.

*Firpene Hydrochloride*,  $C_{10}H_7Cl$ .—Firpene hydrochloride was made by the same method given for the preparation of pinene hydrochloride. After crystallizing several times from alcohol the substance had a melting-point of  $130-131^{\circ}$ , the same as pinene hydrochloride, but differing from the latter by being more volatile and more soluble in nearly all the common solvents and having a slightly different odor. From chloroform and carbon tetra-

chloride, it is amorphous. Chlorine determinations gave the following:

1. 0.2760 gram substance gave 0.22723 gram of AgCl.

2. 0.2704 gram substance gave 0.22143 gram of AgCl.

Calculated for  $C_{10}H_{16}HCl$ : Cl, 20.55. Found: Cl, 20.39 and 20.25.

*Firpene Dichlorhydrochloride*,  $C_{10}H_{14}Cl_2HCl$ .—Firpene hydrochloride differs widely from pinene hydrochloride in its chemical properties, especially when treated with chlorine. Pinene hydrochloride will not form a dichlorhydrochloride but forms with excess of chlorine the hexachlorhydrochloride. Firpene hydrochloride on the contrary readily forms a dichlorhydrochloride, but repeated attempts to make higher chlorides were unsuccessful, the dichloride being always formed. The dichloride proved to be less volatile and less soluble in alcohol than the hydrochloride and more soluble than the pinene pentachloride.

Analysis gave 44.21 per cent. Cl; calculated for  $C_{10}H_{16}Cl_2HCl$ , 44.04.

*Firpene Hydrobromide*,  $C_{10}H_{16}HBr$ .—Firpene forms a well crystallized hydrobromide which differs entirely from the pinene hydrobromide. The method of preparation was the same as that used in the preparation of the hydrochloride. Thoroughly dried hydrobromic acid gas was passed into a chloroform solution of firpene. The crystalline substance was purified by recrystallizing from alcohol. The pure substance had a melting-point of  $102^{\circ}$ . The hydrobromide of pinene melts at  $90^{\circ}$ . The crystals seem to have a feathery form, are readily pressed into a gummy mass and are very volatile. It has a pronounced odor of camphor. It is soluble in nearly all the common organic solvents.

Bromine determinations gave 36.98 per cent. Br; calculated for  $C_{10}H_{16}HBr$ , 36.86 per cent.

*Behavior of Pinene and Firpene with Nitrosyl Chloride*.—One of the most characteristic and easily prepared compounds of pinene is the nitrosylchloride. The method given by Wallach<sup>1</sup> was followed to the letter with both pinene and firpene. The former gave without difficulty a fine crystalline substance while the latter gave no crystalline compound even after repeated trials. A small quantity of an oily substance obtained from firpene may have possibly been a nitrosochlor compound. In fact, this reaction seems to be a characteristic of firpene as well as of pinene.

<sup>1</sup> Ann. 253, 251; 245, 251.

The chlorine compounds made thus far are oils, no matter how much or how little chlorine has entered the compound. These oils are difficult to purify inasmuch as all of them decompose before the boiling-point is reached. We have had several compounds in hand but have as yet been unable to purify them. On the contrary both firpene and pinene when first converted into the hydrochlorides, form crystalline compounds of chlorine, the melting-point rising with the increase of chlorine until the decachlor compound is reached. Substitution products from these various chlorides are now in preparation.

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## THE PITCH AND THE TERPENES OF THE NORWAY PINE AND THE DOUGLAS FIR.

BY G. B. FRANKFORTER.

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PRELIMINARY.

IT HAS been known for several years that the Norway pine and the Douglas fir are rich in the terpenes and resin. During a few days in the spring, the Norway pine seems almost as rich in pitch and turpentine as its southern sister species but the conditions are such that "boxing" as practised in the south is out of the question. A series of "boxing" experiments resulted in collecting a considerable quantity of pitch for chemical examination and incidentally proved the impracticability of this method in the north. Although boxing does not seem practicable in the north and west, so far as I have been able to determine, the reason seems to be largely due to climatic conditions so that if the pitch and turpentine of the north and west are to be utilized, other methods than the common method of the south must be employed.

At the present time, nothing has been done by the lumbering industries either in the north or west toward utilizing the large amount of waste pitchy material. As a result, enormous quantities of wood, too rich in pitch to be of any value to the lumbering industries are burned or thrown aside as worthless. The enormous profits in lumber have made it unnecessary for lumbering industries to look to any of the by-products in order to earn large dividends on capital invested. As a natural consequence



no effort has been made by these corporations to utilize the waste products, and to produce pitch and turpentine in the north.

At the present time, practically all the turpentine used in the north and west comes from the south. The small quantity made in the north and west is scarcely worth considering. The tars and resins likewise come almost wholly from the south and from foreign countries. The rapid increase in the demand for these products has increased the already rapid destruction of the forests of the south to such an extent that at the present rate of destruction it is only a matter of a few years when the southern forests will be completely destroyed. This condition of affairs makes it absolutely necessary that new and modern methods of orcharding should be resorted to at once and that new fields should be opened by utilizing the waste products regarded at present as worthless. The United States Department of Agriculture has already fully realized the present conditions and has sounded a warning through one of its officials, Dr. Charles H. Herty, who in an admirable paper on "Turpentine Orcharding," shows that the southern industry will disappear in the near future unless the present methods are radically changed. That new fields may be developed seems both essential and certain, but much pioneer work must yet be done before these new fields become producers of turpentine, colophonium and tar.

This work was begun several years ago with the object of studying the northern turpentine problem from the industrial standpoint and especially with the idea of comparing the products of these hitherto unknown species with those of the south from the chemical point of view. The red or Norway pine, *Pinus resinosa*, and the Douglas fir or spruce, *Pseudotsuga taxifolia*, on account of their abundance, have been taken up first. Other important species will be taken up later.

Both of the above-named species contain considerable pitch but neither will yield an appreciable quantity by the "boxing" method of the south. Of these two species, the Norway comes the nearer to the southern pine, but the fir wood is on the whole a little richer in both resin and in turpentine than the Norway pine.

*The Norway Pine.*—The so-called "northern pine," or *Pinus resinosa*, is one of the important species of the north. It is one of the two great lumbering species of the northwestern states. The "white pine," the other species, is preferable for lumber on

account of the smaller amount of resin it contains, but the northern pine is sought after because the trees are, as a rule, larger. It very seldom happens that a tree is so full of pitch that it can not be used for lumber, although frequently trees are found to contain so much pitch that the lumber can only be used for certain purposes.

During the past twelve years the problem of recovering the pitch from the Norway pine has been studied. It was found that, during the winter months when the lumbering firms fell most of their timber, the pitch is largely in the lower part of the trunk and in the roots. It seemed, therefore, that the greater part of the pitch might, in some way, be extracted from the stumps and from the waste material in the lumbering business. This has been the prime object of the experiments which are given below.

So far as could be ascertained, the northern pine had not been studied when this work was begun several years ago. Professor Henry Trimble, in a monograph on the pine family, briefly refers to one of the above-named species but no systematic work was done on it further than the study of the twigs and needles together with a brief examination of the wood itself. Nothing definite was known either of the amount of pitch in the wood or of the amount of turpentine in the pitch. Through kindness of the Weyerhaeuser Lumber Company,<sup>1</sup> the writer was able to obtain a quantity of water-white pitch just as it came from the trees by the "boxing process." This and the pitch obtained from the stumps and other waste material have been examined. The pitch from the stumps was recovered by extraction, by steam distillation and by slow destructive distillation. From these experiments, it is evident that in the near future, these waste products will be utilized, not only in the production of the turpentine but also of tar and other by-products.

Among the problems to be solved were, first the amount of colophonium and turpentine present in the various grades of wood, and second a method for the saving of these products.

That the exact amount of pitch might be ascertained, a large number of determinations were made on the various samples of wood, ranging from the richest to the poorest in pitch. Various

<sup>1</sup> I am especially indebted to Mrs. J. R. Jewett, through whose influence the first Norway pitch was collected in any quantity.

methods were used in the extraction. The following numbers are averages of several determinations each :

Lean wood gave an average of 6.2 per cent. of pitch.

Average wood gave an average of 8.6 per cent. of pitch.

Stumps gave an average of 19.4 per cent. of pitch.

Pitchy wood gave 39.1 per cent. of pitch.

Very pitchy wood gave 42.6 per cent. of pitch.

*Properties of Norway Pitch.*—Norway pitch obtained from the trees by boxing is colorless and mobile while that obtained from the wood by extraction with the common solvents is slightly colored, otherwise their properties are identical.

Specific gravity of Norway pitch at 20°, 0.8137.

Index of refraction, 1.47869.

Optical activity at 20° is  $(\alpha)_D = +4^\circ$ .

The pitch as obtained by the above methods of extraction contains about one-fifth of its weight of turpentine, the remainder being colophonium or resin with a very small quantity of water. An average of five determinations gave the following :

Percentage of turpentine, 22.1 ; percentage of colophonium, 77.3 ; percentage of water, 0.6.

When exposed to the air the pitch loses turpentine so that after a month or two it becomes a semisolid or solid, depending upon the amount of turpentine remaining.

The colophonium has already been studied and the report on the work will follow this paper.

*Fir Wood.*—The Douglas fir is to the western states what the Norway pine is to the northern and the yellow pine is to the southern states. The species is interesting on account of the enormous size which it attains and on account of the wide variation in the amount of pitch which it contains. Owing to the high specific gravity of the pitchy wood, a series of specific gravity determinations was made on samples lean and rich in pitch, with the following results :

	Fir.	Norway.
Lean wood, sp. gr. at 20°, average of 5 tests.....	0.6074	0.6025
Medium wood, sp. gr. at 20°, average of 5 tests.....	0.6711	0.6432
Fat wood, sp. gr. at 20°, average of 5 tests ..	0.8225	0.7984
Very fat wood, sp. gr. at 20°, average of 5 tests.....	0.9456	0.9122
Roots (green), sp. gr. at 20°, average of 5 tests.....	0.9746	0.9321

*Fir Pitch.*—The Douglas fir likewise varies widely in the quantity of pitch. It frequently happens that fir logs are so pitchy

as to be worthless for lumber. They are therefore thrown away or burned. In order to determine the quantity of pitch in various grades of wood, a series of determinations was made by extracting with the various solvents and evaporating so as to avoid loss of the turpentine. The richest and the poorest samples of wood were selected for examination.

An average of five determinations in each of the samples given below, gave the following results:

Very lean wood gave 11.6 per cent. of pitch.

Lean wood gave 13.5 per cent. of pitch.

Medium wood gave 19.8 per cent. of pitch.

Rich wood gave 40.7 per cent. of pitch.

Very rich wood gave 42.4 per cent. of pitch.

*Properties of Fir Pitch.*—Fir pitch as it runs from the trees is a perfectly clear liquid varying somewhat in its properties. Usually it is water-white and quite mobile. On exposure to the air it changes its color and slowly becomes viscous. This change is due, as in the case of the Norway pitch, to loss of turpentine and to slow oxidation.

The water-white pitch was collected directly from the tree, placed in a closed vessel, so as to prevent oxidation, and kept in this condition until examined. On exposure to the air it was found to change. White pitch had the following properties: It is colorless with a peculiar aromatic odor.

Sp. gr. at 20°, 0.9821.

Index of refraction at 20°, 1.51745.

Optical activity ( $\alpha$ )<sub>D</sub> = -8.82.

At a freezing temperature it is a solid, gradually changing until at 15° it is quite mobile. The amount of turpentine in the fir pitch was about 22 per cent., or the same as in the Norway pitch.

*The Terpenes.*—The terpenes from the Norway pine and the Douglas fir have been studied. They have been obtained from the pitch which had been recovered by "boxing" and from the pitch which had been extracted from the wood by the various solvents. In addition to these methods, they were obtained from the wood by destructive distillation. In each case it was found that the terpenes obtained by destructive distillation differed from those which were obtained from the wood and from the pitch by steam distillation or by extraction from the wood. Those

obtained from the wood by steam distillation and extraction seem to be of simpler nature than those obtained by destructive distillation. The terpenes obtained by destructive distillation have a wide variation of boiling-points, ranging from  $149^{\circ}$  to  $208^{\circ}$ . Even the properties of the compounds of the same boiling-points seemed to have been changed during the process of destructive distillation. The following is a comparison of the two terpenes.

	Norway terpene		Fir terpene	
	Steam Dist.	Destructive Dist	Steam Dist	Destructive Dist
Specific gravity at $20^{\circ}$ .....	0.8636	0.8666	0.8621	0.8662
Boiling-point.....	$153-154^{\circ}$	$158-160^{\circ}$	$153.5-154^{\circ}$	$157-160^{\circ}$
Index of refraction at $20^{\circ}$ ...	1.47127	1.4716	1.47299	1.47246
Optical activity..... $(\alpha)_D = +17.39-7.56^{\circ}$			-47.2	-29.4 $^{\circ}$

These terpenes are now being studied.

UNIVERSITY OF MINNESOTA

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON OILS AND EXTRACTS.

BY EDWARD MACKAY CHACE

Received July 13, 1906

THE detection of the adulteration of lemon oils and extracts is a problem that has long been disturbing those chemists who are engaged in food and drug analyses. Methods for the detection of the crude forms of adulterations have been devised and are in the main satisfactory. Unfortunately, as the lemon oil industry has developed, certain by-products have come into existence and in the effort to cheapen the cost, these products have been used to produce a grade of impure oil.

With the introduction of these oils the detection of factitious oils and extracts has become a more difficult matter. When the adulteration consisted in the addition of foreign substances such as turpentine or of the substitution of other oils for lemon oil, determinations of the physical constants of the sample and of the first fractions of its distillate were generally sufficient. Now, however, when it consists in varying the proportion of the constituents themselves, physical constants alone are not sufficient.

Lemon oil is composed of 90 per cent. *d*-limonene, 4 to 6 per cent. citral, the remainder being other aldehydes and oxygenated bodies.

It will be readily seen that the physical constants of citral would have to be greatly different from those of lemon oil in order that its partial removal could be detected. As a matter of fact, in their optical activity the two are markedly different, citral being inactive while lemon oil has a rotation of  $+60^{\circ}$  at  $20^{\circ}$ . Methods, however, depending upon the polarization of the oil before and after the removal of the citral have not been brought to a satisfactory state of perfection, probably on account of the difficulty of freeing the oil from citral. The citral sulphite compound has a tendency to split up in the presence of the alkali formed in the reaction.

As for chemical methods no satisfactory method has yet been devised for the determination of any of the constituents. Many attempts have been made to perfect methods for estimating citral but all have serious faults affecting their accuracy. Little or no work has been done toward amplification or improvement of the methods on lemon extracts since the work of Mitchell<sup>1</sup> although attention has been called to the need of a method for citral.

The method which is described in the following pages was an attempt toward the determination of citral in lemon oil, but the error made in comparing the solution and standard becomes so great when multiplied to correct for the dilution that it somewhat impairs the usefulness of the method for oils. On extracts the conditions are different and nothing is wanting in the way of accuracy. Medicus in 1895<sup>2</sup> published an article on the determination of aldehydes in distilled liquors, this method depending upon the recoloration of a solution of fuchsin in sulphurous acid. Tolman testing this method while working on whiskies in this bureau discovered that it was essential that the color should be developed at a low temperature.

In modifying the method to admit of its use on lemon oils this fact was verified. It was at first thought that the reagent would have to be made up in alcohol on account of the insolubility of lemon oil. No satisfactory way of preparing an alcoholic reagent was discovered, however. The reagent finally used is similar to that of Medicus but containing a much larger quantity of sulphurous acid. The method as modified is as follows: Reagents, aldehyde, free alcohol 95 per cent. by volume. The alcohol was

<sup>1</sup> This Journal, 21, 1132 (1899).

<sup>2</sup> Forch. Ber. Lebensm. 1895, 299.

allowed to stand over alkali for several days, distilled, and the distillate boiled for several hours under a reflux condenser with 25 grams per liter of metaphenylenediamine hydrochloride and finally distilled. After this treatment it contains only minute traces of aldehydes.<sup>1</sup> Fuchsin solution: Dissolve 0.5 gram of fuchsin in 100 cc. of water and add a solution of sulphurous acid containing 16 grams of sulphur dioxide. Allow to stand until decolorized and make up to one liter. This solution deteriorates on standing and should therefore be made up every two or three days.

Standard citral solution: Dissolve 1 gram of chemically pure citral and make up to one liter with 50 per cent. by volume alcohol. The citral used was obtained from Schimmel & Company, guaranteed chemically pure. Its physical constants corresponded to those of pure citral. Two samples purchased at different times were identical. Manipulation: While in use all reagents were kept in a water-bath cooled to 15°, and all comparison tubes were left in the bath for ten minutes before the comparison was made. A bath such as was described by Given<sup>2</sup> was used.

For lemon oil 2 grams of the sample were weighed and transferred to a 100 cc. flask with alcohol, cooled to 15°, and made up to the mark. For lemon extracts a larger amount was necessary, usually 20 to 30 grams. Aliquot portions of this solution, about 4 cc. measured at the temperature of the bath, were placed in comparison tubes, 20 cc. of the aldehyde-free alcohol added, then 20 cc. of the fuchsin solution and finally made up to 50 cc. with the alcohol. Comparison tubes were prepared in the same way taking 4 cc. of the standard solution. All the tubes, after mixing, were allowed to remain in the bath for ten minutes, when they were removed and the comparisons made either by direct matching or by the use of a colorimeter. When a colorimeter was used which read percentages of color as compared with the standard, a correction had to be made, owing to the fact that the color developed was not proportional to the amount present. This correction varies somewhat with the conditions under which the samples are worked. In order to avoid it, the first sample weighed out was used as a trial estimation, a second sample being used for the correct determination. The amount weighed for this sample was sufficient to give the solution approximately the same strength

<sup>1</sup> For another method see Dunlap: *This Journal*, 28, 395.

<sup>2</sup> *This Journal*, 12, 1519 (1905).

as the standard, *i. e.*, 1 mg. citral per cubic centimeter, using the trial determination as a basis for the calculation. The readings on the second sample were usually so close as not to require a correction. Two or three comparisons were made on this solution and the average taken. The color developed by the lemon oil is not exactly the same shade as that developed by citral. This fact may be due to the presence of citronellal, as the color is not altered by the addition of limonene to the standard.

To test the accuracy of the method the following determinations were made. A sample of limonene containing some citral was used as a base and several samples made by adding known quantities of citral. The method was also tried on solutions of citral and on lemon oil. Four determinations were made on the limonene as follows: A, 2.27 per cent.; B, 2.31 per cent.; C, 2.41 per cent.; D, 2.36 per cent.; average, 2.34 per cent. citral. Sample A was composed of 97 grams of the limonene and 3 grams of citral having in all 5.28 grams of citral per 100 grams. Two determinations were made, both giving 5.29 per cent. citral. Sample B contained 5.46 grams of citral in 94.54 grams of citral-free limonene making it contain 5.46 per cent. Four determinations resulted as follows: 5.74, 5.82, 4.90, 4.87 (the poor results here can only be accounted for by the fact that the fuchsin sulphurous acid solution was too old for accurate use). Sample C contained 20.85 grams of a terpene containing 0.25 per cent. of citral or 0.0521 gram, to which were added 1.0075 gram citral, making the oil contain 4.85 per cent. Five determinations gave a minimum of 4.90 per cent., maximum of 5.21 per cent., average 5.05 per cent. Sample D, 97.83 grams limonene containing 0.225 gram citral and 4.63 grams of added citral, the whole containing 7.71 per cent. citral. Three determinations gave 7.61, 7.57 and 7.62 respectively. Sample E was made up of terpenes containing 0.1150 gram of citral and 0.0770 gram of citral, having 3.78 per cent. of the latter. Three determinations resulted as follows: 3.61, 3.84, 3.47, averaging 3.62.

Lemon extracts were made up as follows:

	Gram citral per 100 cc.	Found.
A.....	0.1065	0.1092
B.....	0.1060	0.1110
C.....	0.0968	0.1071
D.....	0.30	0.282
E.....	0.12	0.129
F.....	0.25	0.23



A great many other determinations were made on known samples and as stated above. Satisfactory results were always obtained in the case of lemon extracts, while the results on oils were not so good. The maximum error on oils was usually less than 0.5 per cent. while the average was in the majority of cases within 0.2 per cent.

The essential point to be observed in using the method is to keep the temperature of the reagents and the comparison tubes down to at least 15°, and give the standard and sample exactly the same treatment throughout.

[CONTRIBUTION FROM THE FOOD DIVISION OF THE BUREAU OF CHEMISTRY,  
U. S. DEPT. OF AGRICULTURE SENT BY H. W. WILEY.]

## ESTIMATION OF SUGARS BY MEANS OF THE REFRACTOMETER.

BY L. M. TOLMAN AND W. B. SMITH

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IN A great many materials such as syrups, molasses, and similar substances which are for all practical purposes solutions of sugar and water, the estimation of sugar has long been made by determining the specific gravity with a hydrometer or pycnometer and from the specific gravity calculating the percentage of sugars from a table or by some formula

This figure, if the solution is a mixture of a pure sugar and water, can be very accurately determined but in syrups and molasses which are impure mixtures, it represents more nearly a determination of the total substances in solution or the total solids. The determination of total solids is a very important one in a great many food products as a check on the other determination and it is for work of this kind that the specific gravity is of value. The accuracy of the specific gravity method in a mixed sugar solution such as we ordinarily have to deal with, depends on the fact that the different sugars have very nearly the same specific gravity for the same concentration. The specific gravity method is also especially useful with substances which are decomposed by drying at a high temperature, such as solutions containing large amounts of invert sugar, where results by drying are too low.

The index of refraction is a figure of practically the same value as the specific gravity in solutions of the kind mentioned above and has about the same limitations. The index of refraction of solutions of soluble carbohydrates increases regularly with the concentration, and the accuracy of the determination is limited only by the accuracy and sensitiveness of the refractometer. Stolle<sup>1</sup> published some results on the index of refraction of sugar solutions using the Pulfrich refractometer and showed that with sucrose, *d*-glucose, *δ*-*l*-fructose ("levulose") and lactose, there was little variation in the reading of the refractometer with solutions of the same concentration and that very accurate results could be obtained with pure sugar solutions. He also demonstrated that the relation between the index of refraction and specific gravity as calculated by the Lorenz formula  $\frac{N_2 - 1}{(N_2 + 2)D}$  was a constant, 0.206, thus showing that the same results can be obtained by the index of refraction and the specific gravity.

The following work was undertaken to test the value and accuracy of the Abbé refractometer for this kind of work, to check up Stolle's work, and to complete the list of sugars, as he had no figures on maltose, commercial glucose, or the other soluble component of glucose, that is dextrin, which is often an ingredient of the commercial products on the market.

The instrument used was the new form of the Abbé refractometer with a water-jacket prism so that the temperature at which the readings were made could be exactly regulated. The index of refraction was obtained in exactly the same manner as when an oil is examined in the same instrument.

The instrument was standardized against a quartz plate with a known index of refraction and against pure water and found to read slightly low, about 0.0004, and the readings were corrected by this factor.

The readings were all made at 20°, using ordinary light and compensating for the dispersion by means of the prisms in the instrument. The sugar solutions were made up by weighing the sugars into a glass stoppered flask and then adding a weighed amount of water so that the results were direct percentages by weight.

<sup>1</sup> Z. Ver. dent. Zucker-Ind. 1901, 335-347 and 469-487.

The moisture in the various sugars was determined by drying at  $70^{\circ}$  to constant weight and at a diminished pressure of about 27 inches. It can be seen that a method of this kind would have many advantages in inspection work—the ease and rapidity with which a determination can be made and the ease and accuracy with which the temperature can be regulated as well as the small amount of sample needed for the determination give it many advantages over the specific gravity method.

The following curve shows graphically the results obtained with the various sugars.

The curve is drawn from the results obtained with sucrose up to a concentration of 65 per cent. from which point it was extended by calculation to 90 per cent. The points for commercial glucose between 80 and 90 per cent. were determined by readings with four different glucoses and they were found to coincide exactly with the calculated curve for sucrose; determinations with glucose of other concentrations, as shown on the curve, also coincide with the sucrose line.

The other sugars examined were maltose and lactose which are also on the sucrose curve, showing that for practical purposes all these sugars have the same index of refraction for the same concentration and that a table prepared for sucrose will be satisfactory for all.

The only other soluble carbohydrate examined was dextrin which, as is shown on the curve, has a slightly higher index of refraction. The close agreement between sucrose and commercial glucose, which is a mixture of dextrose, maltose, and dextrin, is due to the fact that dextrose and maltose have an index of refraction very slightly lower than sucrose while dextrin is slightly higher, the resultant being practically that of sucrose. The following table shows better than the curve, which is not on a sufficiently large scale, the difference between the various sugars.



TABLE I.—INDEX TO REFRACTION OF VARIOUS SUGARS OF DIFFERENT CONCENTRATION.

Dried in vacuum at 70° C. to constant weight.

Index of Refraction 20° C.	Sucrose. Per cent.	Maltosa. Per cent.	Commercial glucose. Per cent.	Lactose. Per cent.	Dextrin. Per cent.	Stolle. <i>d</i> -Glucose. Per cent.	<i>δ</i> - <i>l</i> -Fructose. Per cent.
1.3343	1.00	1.00	1.00	1.00	1.00	1.00	1.14
1.3357	2.00	2.07	2.00	2.00	1.93	1.80	2.07
1.3402	5.00	5.07	5.00	5.13	4.87	5.13	5.13
1.3477	10.00	10.07	10.07	10.13	9.60	10.13	10.13
1.3555	15.00	15.12	15.06	15.13	14.13	15.19	15.19
1.3637	20.00	20.17	20.06		18.94	20.29	20.24
1.3722	25.00		25.00		23.71	25.47	25.47
1.3810	30.00		30.02		28.78		
1.3902	35.00		35.03				
1.3997	40.00		40.05				
1.4096	45.00		45.04				
1.4200	50.00		50.03				
1.4306	55.00		55.02				
1.4419	60.00		60.01				
1.4534	65.00		65.01				
1.4653	70.00		70.00				
1.4776	75.00		75.00				
1.4903	80.00		80.00				
1.5034	85.00		85.00				
1.5170	90.00		90.00				

Taking sucrose as the standard, the other sugars in concentrations up to 20 per cent. show practically no difference in the reading on the refractometer. A reading of 1.3637 is equivalent to 20 per cent. of sucrose, 20.17 of maltose, 20.06 per cent. of commercial glucose, 20.29 per cent. of *d*-glucose, 20.24 per cent. of *δ*-*l*-fructose and 18.94 per cent. of dextrin. Dextrin alone of all the substances examined differs appreciably from sucrose, it having a slightly higher index of refraction.

The index of lactose is also very close to that of sucrose so that in most cases the same table can be used for all of the sugars in the same way that the Brix table is used for specific gravity determinations. The following table for the value of the index of refraction for sucrose for each per cent. up to 90 per cent. has been calculated from the curve, and for ordinary work this will be found satisfactory for all sugars.

TABLE II.—INDEX OF REFRACTION OF SUCROSE.

Sucrose. Per cent.	Index of refraction 20° C.	Sucrose. Per cent.	Index of refraction 20° C.	Sucrose. Per cent.	Index of refraction 20° C.
1	1.3343	31	1.3828	61	1.4442
2	1.3357	32	1.3847	62	1.4465
3	1.3372	33	1.3865	63	1.4488
4	1.3387	34	1.3883	64	1.4511
5	1.3402	35	1.3902	65	1.4534
6	1.3417	36	1.3921	66	1.4557
7	1.3432	37	1.3940	67	1.4581
8	1.3447	38	1.3959	68	1.4605
9	1.3462	39	1.3978	69	1.4629
10	1.3477	40	1.3997	70	1.4653
11	1.3492	41	1.4017	71	1.4677
12	1.3508	42	1.4036	72	1.4701
13	1.3524	43	1.4056	73	1.4726
14	1.3539	44	1.4076	74	1.4751
15	1.3555	45	1.4096	75	1.4776
16	1.3572	46	1.4117	76	1.4801
17	1.3588	47	1.4137	77	1.4826
18	1.3604	48	1.4158	78	1.4851
19	1.3621	49	1.4179	79	1.4877
20	1.3637	50	1.4200	80	1.4903
21	1.3654	51	1.4221	81	1.4929
22	1.3671	52	1.4242	82	1.4955
23	1.3688	53	1.4263	83	1.4981
24	1.3705	54	1.4284	84	1.5007
25	1.3722	55	1.4306	85	1.5034
26	1.3739	56	1.4328	86	1.5061
27	1.3756	57	1.4351	87	1.5088
28	1.3774	58	1.4373	88	1.5115
29	1.3792	59	1.4396	89	1.5142
30	1.3810	60	1.4419	90	1.5170

In order to correct for different reading temperatures, the following table was prepared, readings being made on the same solutions at 20°, and at 30°, and on concentrations varying from 2 per cent. to 62 per cent.

TABLE III—CORRECTION FOR TEMPERATURE.

Percentage of sugar.	Index at 20° C.	Index at 30° C.	Difference.	Correction for 10° in per cent. sugar.	Correction for 10° in per cent. sugar, from Brix table.
2.18	1.3358	1.3348	0.0010	0.66	0.64
7.43	1.3438	1.3428	0.0010	0.66	0.67
15.82	1.3569	1.3557	0.0012	0.70	0.70
51.71	1.4236	1.4219	0.0017	0.81	0.79
62.52	1.4477	1.4459	0.0018	0.78	0.76

The differences were calculated to per cent. of sugar and compared with the correction for temperature used in specific gravity work, the Brix table for correction for temperature being used. The results show that the temperature correction for the specific gravity and the index of refraction are practically the same and the table as given for Brix can be used for the index of refraction. The manner of using the table is the same. The reading of index of refraction is made at room temperature and this reading calculated to per cent. of sugar, then the proper correction from the table calculated and applied.

In the Brix table for correction for temperature the maximum correction is at a concentration of about 50 per cent. and, as will be seen from the table above, this same fact is noted in the temperature correction for index of refraction.

In conclusion: It appears from this work that the refractometer is a satisfactory instrument for determining the soluble carbohydrates in solution under the same conditions as those under which specific gravity can be used, and in fact it gives the same results; that it has many advantages over the specific gravity method in speed, ease of manipulation and amount of sample required for the determination; that for a great deal of work where quickness and approximate accuracy only are necessary, the refractometer will be used. The butyro-refractometer is of no value for this work as its range of readings does not take in sugar solutions below 50 per cent. of sugar.

## THE OPTICAL ROTATION OF GLIADIN IN CERTAIN ORGANIC SOLVENTS.

BY W. E. MATHEWSON.

Received August 4, 1906.

THE experiments given here were carried out in connection with an investigation, the object of which was to effect some improvement on the present methods of flour analysis. The work has been interrupted so it has been thought best to publish these results.

The gliadin used was prepared from a bakers' grade hard wheat flour by extracting with 60 per cent. alcohol, filtering the extract until perfectly clear, concentrating and precipitating with absolute alcohol. The crude gliadin thus obtained was again dissolved and precipitated, digested repeatedly with ether and finally dried

over sulphuric acid. All alcohol and ether used had been carefully redistilled. The preparation was soluble to a perfectly clear and almost colorless solution in dilute alcohol. Duplicate portions contained 17.42 per cent. and 17.52 per cent. of nitrogen, determined by the Gunning method, the digestion being continued for two hours after the mixture had become colorless. It was thoroughly mixed during and after the drying so that the nitrogen determinations might be consistent with the polarimetric observations. It is very probable that the proteid was not quite free from moisture; and the specific rotations obtained have been corrected by multiplying by the factor  $1766/1747$ .

The gliadin was soluble in dilute methyl and propyl alcohols, and in glacial acetic acid, phenol, paracresol and benzyl alcohol. A white precipitate, presumably gliadin, was produced when the phenol solution was treated with ether, acetone or pyridine, and somewhat less readily when treated with benzene or chloroform. Pure methyl, ethyl, propyl and amyl alcohols produced precipitates, the amount required being less, the greater the molecular weight of the alcohol. No turbidity followed the addition of several volumes of aniline, phenylhydrazine, or nitrobenzene, but when gliadin was treated with these substances it did not seem to dissolve, and the clear filtrates showed practically no optical activity. It seemed somewhat soluble in benzaldehyde, but the sample of the latter used was not pure.

In order to ascertain whether the gliadin underwent decomposition on dissolving in phenol, about 7 grams were taken, dissolved in about 100 cc. hot phenol and the solution, after cooling, poured into about 500 cc. pure benzene. A heavy precipitate was produced, although the addition of a little of the supernatant liquid to benzene caused a further separation of solid material, showing that a considerable amount still remained dissolved. The liquid was decanted off, the precipitate washed repeatedly with benzene, drained with suction and dried for three weeks over sulphuric acid *in vacuo*. It still retained a faint odor of phenol. Two portions were taken, dissolved in 70 per cent. ethyl alcohol, and the solutions polarized. The latter were not absolutely clear but were sufficiently clear to enable saccharimeter readings to be obtained without difficulty. Ten cc. were taken from the saccharimeter tube and the nitrogen content determined. From this the specific rotation was calculated, assuming



the gliadin to be equal to the nitrogen multiplied by 10000/1766. The following are the data:

Saccharimeter reading, 40° C. 100 mm. tube.	Grams of nitrogen in 100 cc. at 40° C.	$[\alpha]_D^{40}$ V.
-4.53° V.	0.3051	-90.95
-5.45° V.	0.3678	-90.76

The specific rotation of the substance seems to have suffered but little change. It gave the biuret reaction and the red-purple coloration with diluted sulphuric acid exactly as does pure gliadin. A solution of gliadin in phenol, giving a saccharimeter reading of -19.7° V (200 mm. tube), was sealed up in a glass bulb and maintained at a temperature of about 140° in an air-bath for three and one-half hours. It then gave a reading of -18.4° V.

The solutions of gliadin in glacial acetic acid and in benzyl alcohol gave precipitates with ether exactly resembling gliadin in appearance, and which dissolved readily in dilute alcohol. These latter solutions gave the biuret reaction.

The specific rotations of the gliadin were obtained with a triple shadow saccharimeter, a jacketed tube being used for the solution. The following are the data:

Solvent.	Grams gliadin per cc. at 40°	Saccharimeter reading in Ventzke degrees.	$[\alpha]_D^{40}$ . Degrees.
Methyl alcohol, 70 per cent....	0.03644	-19.81	-95.3
Methyl alcohol, 70 per cent....	0.03366	-18.42	-96.0
Ethyl alcohol, 70 per cent.....	0.03085	-16.21	-92.1
Ethyl alcohol, 70 per cent.....	0.04499	-23.55	-91.8
Ethyl alcohol, 60 per cent .....	0.02264	-12.52	-96.9
Ethyl alcohol, 60 per cent .....	0.02388	-13.13	-96.4
Ethyl alcohol, 60 per cent.....	0.03126	-17.25	-96.7
Ethyl alcohol, 50 per cent.....	0.02895	-16.29	-98.6
Ethyl alcohol, 50 per cent .....	0.04914	-27.55	-98.3
Propyl alcohol, 60 per cent ...	0.02990	-17.07	-100.9
Propyl alcohol, 60 per cent ...	0.03015	-17.42	-101.3
Phenol, 70 per cent .....	0.02035	-14.25	-122.7
Phenol, 70 per cent .....	0.03340	-23.56	-123.6
Phenol, anhydrous.....	0.02824	-21.31	-132.2
Phenol, anhydrous.....	0.03018	-22.73	-132.0
Phenol, anhydrous.....	0.04288	-32.07	-131.1
Paracresol.....	0.02799	-19.54	-121.0
Glacial acetic acid .....	0.04267	-19.69	-80.9
Glacial acetic acid .....	0.05014	-22.48	-78.6
Benzyl alcohol.....	0.02282	-6.91	-53.1
Benzyl alcohol.....	0.03050	-10.14	-58.3

The methyl and propyl alcohols and the phenol used were the chemically pure grades from well-known manufacturers and were

fractionated before use. The acetic acid and cresol were chemically pure grade but were not further purified. The benzyl alcohol was fractionated. It had a boiling-point of about  $202^{\circ}$  (uncorrected). The aromatic compounds were tested for optical activity.

The divergence in the results obtained with the benzyl alcohol is doubtless due to the decomposition of a part of the proteid by the heating necessary to bring it into solution. The sample giving the lower reading was purposely kept at a high temperature considerably longer than the other to see if the rotation would be markedly changed. Doubtless the other determinations are also affected with some error due to the same cause, although this was guarded against as far as was practicable.

The fact that gliadin is soluble in phenol would seem to render possible an approximate determination of its molecular weight by the freezing-point method. Since it is also soluble in boiling 70 per cent. propyl alcohol, a determination by the boiling-point method might be made since G. N. Lewis has shown<sup>1</sup> that Raoult's law regarding the elevation of the boiling-point can be applied to a binary solvent whose vapor has the same percentage composition as the liquid. The presence of traces of moisture would affect the results by the latter method much less, although gliadin is doubtless more or less altered by continued warming with any solvent containing water.

An attempt has been made to estimate the gliadin present in flour by digestion with phenol and polarization of the filtered extract. The results obtained seem to indicate that a quite complete extraction of the gliadin is effected. It is possible, however, that more or less glutenin also dissolves in the phenol. The chief difficulty encountered is in the filtration of the mixtures.

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## THE SEPARATION OF PROTEOSES AND PEPTONES FROM THE SIMPLER AMINO BODIES.

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OF THE methods that have been employed during recent years for the separation of proteoses and peptones from the simpler

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amino bodies, the following methods have been used most commonly.

First, Stutzer's method<sup>1</sup> by means of precipitation with phosphotungstic acid.

Second, Mallet's method<sup>2</sup> by precipitation with phosphotungstic acid in hot solutions.

Third, Allen and Searle's method<sup>3</sup> by precipitation with bromine.

Fourth, Schjerning's method<sup>4</sup> by precipitation with a tannin salt solution.

It was believed by Stutzer that the method proposed by him separated peptones completely from all of the simpler amino bodies. Since that time it has been shown repeatedly that phosphotungstic acid precipitates some of the meat bases and that the reagent is not suitable for the purpose for which it was first suggested.

The bromine method of Allen and Searle<sup>5</sup> has been shown to be utterly untrustworthy. It decomposes both proteids and meat bases with the liberation of nitrogen. It has been shown by the writers<sup>6</sup> that bromine does not precipitate all of the proteid bodies present, that the amount precipitated under varying conditions is not constant, and that it is possible to so fix the conditions that relative amounts can be secured. It is true that the results are greatly improved by forming the bromine precipitate in the filtrate from the proteoses precipitated by zinc sulphate, the filtrate being diluted with an equal volume of water before precipitation with bromine. Even then, however, the results obtained by the method are far from satisfactory in the presence of a considerable amount of simple amino bodies.

In previous work<sup>7</sup> the writers found the tannin salt method of Schjerning to have some advantages in this separation. Our work with this method, however, has indicated that slight changes of conditions produced marked influences on the results, and it seemed important to study the method with a view to determining whether it were not possible to so fix conditions as to obtain re-

<sup>1</sup> Z. anal. Chem. 34, 568 (1895).

<sup>2</sup> U. S. Dept. Agr., Bureau of Chem., Bull. 54.

<sup>3</sup> Analyst, 22, 258 (1897).

<sup>4</sup> Z. anal. Chem. 39, 545 (1900).

<sup>5</sup> U. S. Dep't. Agr., Bureau of Chem., Bull. 73.

<sup>6</sup> Ibid., Bull. 81.

<sup>7</sup> Ibid., Bull. 90.

sults that were more nearly correct, or at any rate relatively constant. As a result of this work it was found that much more satisfactory and more constant results were obtained by increasing both the tannin content and the salt content of the reagent. Further particulars of our study of the method are given later.

#### COMPARISONS OF THE ACTION OF REAGENTS ON MEAT BASES.

Solutions of a number of simple amino bodies were treated with phosphotungstic acid in hot and cold solutions; with the tannin-salt reagent of the strength previously employed by the writers; and also a stronger tannin salt solution which was found to give more complete precipitation of the proteid bodies. The results of this work are given in Table I.

By consulting Table I it will be seen that with the more dilute tannin salt solution, precipitates were obtained with creatine, trimethylamine and phenylenediamine. These results were confirmed with the stronger solution of tannin salt, except that no precipitate was given with trimethylamine when the stronger solution was used. The weaker solution also gave a slight turbidity, but insufficient to indicate the precipitation of a determinable amount of nitrogen with glycocoll, alanine, glutamic acid, creatine and glutamine. It is probable that failure to obtain this turbidity with the stronger tannin salt solution is due to the increased difficulty of detecting a turbidity in that solution, and not to the solvent action of the stronger solution on the slight amount of material precipitated by the more dilute solution. Considering the fact that this turbidity was not detected in the stronger solution, and therefore at least was not increased by increasing the strength of the reagent, it is suggested that this was due not to the insolubility of the amino bodies in question in the presence of the tannin salt solution, but rather to a small amount of impurity contained in the preparations examined. It is apparent, however, that creatine and phenylenediamine cannot be separated by this method from peptones. In the case of creatine this is a serious matter, since that substance is the meat base which occurs most abundantly in meat and meat extract.

The error due to creatine, however, can be eliminated by determining the amount of creatine present before and after the pre-

TABLE I.—ACTION OF PROTEID PRECIPITANTS ON AMINO BODIES.

Amino body.	Tannin salt. <sup>1</sup>	Tannin salt. <sup>2</sup>	Phosphotungstic acid, cold.	Phosphotungstic acid, hot (90°C.).
Glycocoll.	Cloud.	None.	None.	None.
Alanine.	Cloud.	.....	None.	None.
Creatine.	Slight ppt.	Rather heavy ppt.	White granular ppt.	None.
Glutamic acid.	Cloud.	None.	None.	None.
Aspartic acid.	None.	None.	None.	None.
Allantoin.	None.	None.	None.	None.
Asparagine.	None.	None.	None.	None.
Betaine.	None.	.....	Flaky white ppt.	None.
Creatinine.	Slight turbidity.	None.	White granular ppt.	None.
Glutamine.	Cloud.	None.	None.	None.
Guanine.	None.	None.	None.	None.
Xanthine.	None.	.....	None.	None.
Hypoxanthine.	None.	.....	White granular ppt.	None.
Leucine.	None.	None.	None.	None.
Trimethylamine.	Heavy ppt.	None.	White ppt. <sup>3</sup>	None.
Diphenylamine.	None.	.....	None.	None.
Phenylenediamine.	Black flaky ppt.	Brown flaky ppt.	A heavy white ppt.	Brownish ppt.
Acetamide.	None.	None.	None.	None.
Sarcosine.	.....	None.	.....	.....

<sup>1</sup> Four grams of sodium chloride and 10 cc. of 12 per cent. tannin per 100 cc.<sup>2</sup> Fifteen grams of sodium chloride and 20 cc. of 12 per cent. tannin per 100 cc.<sup>3</sup> This disappeared on standing 2 or 3 minutes.

cipitation with the tannin salt reagent. The method for this determination is described below. It is believed that phenylenediamine does not occur in meat extract, and that in the examination of meat products, the fact that this substance is precipitated by the tannin salt reagent may be disregarded.

Mixtures of the amino bodies mentioned above were also treated with the same reagents except that in this case the stronger tannin salt solution was not employed, the work having been completed and our samples of amino bodies exhausted before our results indicating the advisability of using the stronger tannin salt solution were obtained. The results obtained by treating the mixtures of amino bodies with the reagents mentioned, as given in Table II, confirm those obtained with the unmixed solutions.

TABLE II — ACTION OF PROTEID PRECIPITANTS ON MIXTURES OF AMINO BODIES.

Amino bodies	Tannin salt <sup>1</sup>	Phosphotungstic acid	
		Cold.	Hot (96° C)
Leucine	} Very slight cloud.	None.	None.
Glycocoll			
Aspartic & glutamic acid.	} Slight cloud.	None.	None.
Acetamide	} None.	None.	None.
Betaine			
Creatine	} Slight cloud.	Heavy white ppt.	None.
Creatinine			
Allantoin	} None.	None.	None.
Asparagine			
Xanthine	} Faint cloud.	Heavy white ppt.	Slight ppt.
Hypoxanthine			
Guanine	} None.	None.	None.
Glutamine			
Trimethylamine	} Heavy yellow brown ppt.	Granular white ppt.	Granular white ppt.
Diphenylamine			

Mixtures were then prepared of two commercial products—Witte's peptone and somatose—consisting largely of proteoses and peptones—with a number of the simple amino bodies, and treated with the reagents mentioned above. The nitrogen was determined in all solutions from which these mixtures were prepared, and the amount of nitrogen contained in the proteose or peptone body and in the simple amino bodies, as well as the

<sup>1</sup> Four grams of sodium chloride and 10 cc. of 12 per cent. tannin per 100 cc.

amount of nitrogen precipitated by the reagent employed, are given in Table III.

TABLE III.—NITROGEN PRECIPITATED BY PHOSPHOTUNGSTIC ACID AND ZINC SULPHATE FROM MIXTURES OF WITTE'S PEPTONE OR SOMATOSE AND AMINO BODIES.

Nitrogen contained and determined.	Witte's peptone. Gram.	Witte's peptone, leucine and tyrosine. Gram.	Leucine and tyrosine precipitated. Gram.	Witte's peptone. Gram.	Witte's peptone, glycocoll, creatinine and creatine. Gram	Glycocoll, creatine and creatinine precipitated. Gram.
Nitrogen content of Witte's peptone or somatose . . .	0.0714	0.0714	.....	0.0762	0.0762	.....
Nitrogen content of solution of amino bodies. . . . .		0.0045 <sup>1</sup>	.....	.....	0.0171	.....
Nitrogen precipitated by phosphotungstic acid. . . .	0.0655	0.0683	0.0028	0.0695	0.0790	0.0095
Nitrogen precipitated by zinc sulphate. . . . .	0.0404	0.0407	0.0003	0.0498	0.0475	.....
Nitrogen contained and determined.	Somatose. Gram.	Somatose, glycocoll, leucine, tyrosine, xanthine, hypoxanthine and guanine. Gram	Glycocoll, leucine, tyrosine, xanthine, hypoxanthine, and guanine precipitated Gram	Somatose. Gram.	Somatose, glycocoll and glutamine. Gram.	Glycocoll and glutamine precipitated. Gram.
Nitrogen content of Witte's peptone or somatose . . .	0.0619	0.0619	.....	0.0619	0.0619	.....
Nitrogen content of solution of amino bodies. . . . .		0.0106	.....	.....	0.0129	.....
Nitrogen precipitated by phosphotungstic acid. . . .	0.0594	0.0637	0.0043	0.0585	0.0604	0.0019
Nitrogen precipitated by zinc sulphate. . . . .	0.0545	0.0547	0.0002	.....	.....	.....

The amount of nitrogen in the portion of Witte's peptone solution taken for examination was 0.0714 gram. Of this amount phosphotungstic acid (Stutzer's method) was found to precipitate 0.0655 gram, and zinc sulphate precipitated 0.0404 gram. To a similar portion of the solution of Witte's peptone was added a solution of leucine and tyrosine containing 0.0045 gram of nitrogen. Of this mixture phosphotungstic acid precipitated 0.0683 gram of nitrogen, and zinc sulphate precipitated 0.0407 gram of nitrogen. The precipitate obtained with zinc sulphate indicates that about two-thirds of the nitrogen present in this sample consisted of

<sup>1</sup> Leucine 0.0025 gram and tyrosine 0.0020 gram.

proteoses. Practically all of the remaining third is probably peptones. By deducting 0.0655 from 0.0683 the amount of nitrogen in the form of leucine and tyrosine precipitated by phosphotungstic acid is given as 0.0028 gram. The results given in this table appear to confirm the qualitative results given in Tables I and II.

ACTION OF TANNIN SALT REAGENT ON MEAT BASES IN THE PRESENCE OF PROTEOSES AND PEPTONES.

The tannin salt reagent was not included in Table III as at the time the work forming the basis of that table was done we had not satisfied ourselves with regard to the conditions under which the method could best be conducted. Similar work with the tannin salt reagent was repeated at a later time, and the results are given in Table IV.

TABLE IV.—NITROGEN PRECIPITATED FROM MIXTURES OF SOMATOSE AND MEAT BASES BY TANNIN SALT REAGENT.<sup>1</sup>

Substance.	Nitrogen in somatose used. Grams.	Nitrogen in amino bodies used. Grams.	Total nitrogen precipitated. Gram.	Amino nitrogen precipitated. Gram.
Blank .....	0.1006	none	0.0966	none
Phenylenediamine ..	0.1006	0.0230	0.1040	0.0074
Creatine .....	0.1006	0.0494	0.1080	0.0114
Creatinine .....	0.1006	0.0090	0.0984	0.0018
Glycocoll .....	0.1006	0.0202	0.0966	none
Sarcosine .....	0.1066	0.0270	0.0956	—0.0010
Allantoin .....	0.1006	0.0348	0.0994	0.0028
Leucine .....	0.1006	0.0034	0.0966	none

Quantities of 0.8 gram each of somatose were mixed with several of the more important meat bases, and the nitrogen determined in the material precipitated by the tannin salt reagent from the mixture. The reagent employed for this purpose was the stronger solution mentioned above; that is, it contained 10 grams of sodium chloride and 4 grams of tannin per 100 cc. of the solution in which the precipitation occurs. The temperature was 12° C.

It will be seen that in only two cases was an appreciable quantity of nitrogen obtained in the precipitate in excess of that obtained with the somatose alone. In the presence of phenylenediamine this was equal to 0.0074 gram of nitrogen, or about one-third

<sup>1</sup> Reagent employed contained 10 grams of sodium chloride and 4 grams of tannin per 100 cc. of the solution in which the precipitation occurred. The temperature was at 12° C.



of the amount present in the amino body. In the presence of creatine containing 0.0494 gram of nitrogen, a little less than one-fourth of that amount, or 0.0114 gram of nitrogen was precipitated by the reagent. In the case of the other amino bodies studied the nitrogen in the precipitate from the tannin salt reagent was so nearly equal to that of the blank that it may be ignored as due to inaccuracies of the method.

#### NITROGEN PRECIPITATED BY VARYING QUANTITIES OF SALT AND TANNIN.

In the presence of a considerable amount of precipitable matter it is impracticable to determine with accuracy the quantity of reagent necessary to make precipitation complete. The amount of reagent was accordingly varied through wide limits for the purpose of determining the amount with which the most complete precipitation of proteid bodies could be obtained. It was found that by increasing the salt solution, even at a concentration far below that at which the precipitation of the ordinary proteids with sodium chloride occurs, the amount of nitrogen precipitated by the tannin salt solution was largely increased. It was also found that a corresponding increase of the precipitate was obtained by increasing the amount of tannin in the solution.

The varying results obtained with different strengths of sodium chloride and tannin suggested the advisability of determining whether there was any degree of concentration for both salt and tannin at which slight changes in concentration would be without material influence upon the results. To determine this the amount of nitrogen precipitated by the tannin salt reagent was determined in solutions whose sodium chloride content varied from 0.8 to 26 grams per 100 cc., and whose tannin content varied from 1.25 to 10 grams per 100 cc.

An inquiry of this sort is greatly complicated, owing to the fact that pure solutions of the proteid bodies can not be obtained. We have found it necessary to study those conditions which would give the maximum results with as pure solutions as were obtainable of proteoses and peptones, and then to use under such conditions solutions of the various meat bases in order to determine whether the latter were precipitated thereby.

An inspection of Tables V and VI will show that approximately the maximum results were obtained by using about 15 grams

per 100 cc. of sodium chloride and 4 or 5 grams per 100 cc. of tannin; that is, the proteid bodies under examination are dissolved in a small amount of water and concentrated solutions of sodium chloride and tannin added in sufficient amount to form solutions of the concentration given above. It also appears from Tables V and VI that a considerable excess of tannin may be employed without any tendency of the reagent to dissolve the precipitate formed in excess.

It is, of course, impossible to determine how completely peptones are precipitated by the tannin salt reagent. It is interesting to know, however, that 15 grams of sodium chloride and 4 or 5 grams of tannin per 100 cc. of solution, which gives the maximum precipitation of proteids, precipitates from 96 to 98 per cent. of the total nitrogen contained in somatose, which from the nature of its preparation is supposed to consist largely of albumoses with a small amount of peptone. With the same reagent we precipitated about 94 per cent. of the total nitrogen contained in Witte's peptone, which is also supposed to consist chiefly of albumoses and peptones, but to contain a larger percentage of peptones than is found in somatose.

It thus appears that maximum precipitations of proteoses and peptones can be obtained from these substances with tannic acid and sodium chloride in the proportion of from 4 to 5 grams of the former and 15 grams of the latter per 100 cc. of the solution in which the precipitation is effected. This, taken into consideration with the fact that minimum precipitations are produced by this reagent with the meat bases, indicates that satisfactory results may be obtained with the reagent.

#### EFFECT OF TEMPERATURE ON PRECIPITATION.

Aliquot portions of solutions containing proteoses, peptones, and simple amino bodies were precipitated with the tannin salt reagent at three temperatures:

First, in a refrigerator at about 12° C.

Second, at room temperature, the precipitate standing over night at about 23° C.

Third, in a drying oven heated with a thermostat, the temperature regulated at about 40° C.

It was found that higher results were obtained with a lower temperature and that the nitrogen precipitated at room tem-

TABLE V.—AMOUNT OF NITROGEN PRECIPITATED FROM ARMOUR'S EXTRACT (TOTAL NITROGEN IN 20 CC. = 0.1780 GRAM)  
BY VARYING AMOUNTS OF TANNIN AND SALT.

(Ice box temperature, 12° C., total volume, 100 cc.)											
Sodium chloride per 100 cc. Grams.		Grams of tannin in varying amounts of 12 per cent. solution used.									
		10 cc = 1.25 grams. Gram.	15 cc = 1.87 grams. Gram.	20 cc = 2.50 grams. Gram.	25 cc = 3.12 grams. Gram.	30 cc = 3.75 grams. Gram.	35 cc = 4.37 grams. Gram.	40 cc = 5.00 grams. Gram.	50 cc = 6.25 grams. Gram.	60 cc = 7.50 grams. Gram.	70 cc = 8.75 grams. Gram.
1.....	0.0831	0.0856	0.0899	.....	0.0921	.....	.....	.....	.....	.....	0.0959
3.....	0.0819	0.0878	0.0900	.....	0.0927	.....	.....	.....	.....	.....	.....
5.....	0.0809	0.0868	0.0887	.....	0.0909	.....	.....	0.0951	.....	.....	0.1015
7.....	0.0825	0.0878	0.0921	.....	0.0964	.....	.....	.....	.....	.....	.....
8.....	0.0826	0.0868	0.0909	.....	0.0909	.....	.....	.....	.....	.....	.....
9.....	0.0831	0.0872	.....	.....	0.0965	.....	.....	.....	.....	.....	.....
10.....	0.0825	0.0873	.....	.....	0.1191	.....	.....	0.0997	.....	.....	.....
11.....	0.0847	0.0906	0.0921	.....	0.0983	.....	.....	.....	.....	.....	.....
13.....	.....	0.0884	.....	.....	.....	.....	.....	.....	.....	.....	.....
15.....	.....	0.0923	0.0937	0.0950	{ 0.0950 0.0999	.....	0.1036	.....	0.1009	0.1043	0.1083
17½.....	.....	.....	0.0982	0.0985		0.0982	0.1070	0.1051	0.1087	.....	.....
20.....	.....	0.0928	{ 0.0967 0.0971	0.0972	.....	.....	0.1060	0.1109	.....	.....	.....
22.....	.....	.....	0.0985	0.1010	.....	.....	.....	.....	.....	.....	.....
23.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
25.....	.....	0.0980	0.1021	.....	0.1079	.....	.....	.....	.....	.....	.....

<sup>1</sup> From this point on in the majority of cases a 24 per cent. solution was used dil to half the resulting strength being the same as that indicated in the table.



TABLE VI.—AMOUNT OF NITROGEN PRECIPITATED FROM 1 GRAM OF SOMATOSE (TOTAL NITROGEN = 0.2149 GRAM) BY VARYING AMOUNTS OF TANNIN AND SALT.

[Temperature 12° C; total volume 100 cc.]

Grams of tannin in varying amounts of 12 per cent. solution used.

Sodium chloride per 100 cc. Grams.	10 cc. = 1.25 grams. Gram.	15 cc. = 1.87 grams. Gram.	20 cc. = 2.50 grams. <sup>1</sup> Gram.	25 cc. = 3.12 grams. Gram.	30 cc. = 3.75 grams. Gram.	35 cc. = 4.37 grams. Gram.	40 cc. = 5.00 grams. Gram.	50 cc. = 6.25 grams. Gram.	60 cc. = 7.50 grams. Gram.	70 cc. = 8.75 grams. Gram.	80 cc. = 10.00 grams. Gram.
0.8.....	0.1014	{ 0.1081 0.1111	0.1086 0.1126	..... .....	{ 0.1092 0.1152 }	..... .....	..... .....	..... .....	..... .....	..... .....	..... .....
1.0.....	.....	.....	.....	.....	.....	.....	.....	0.1167	0.1173	.....	0.1157
2.0.....	.....	.....	.....	.....	.....	.....	.....	.....	0.1161	0.1167	.....
4.0.....	.....	{ 0.1036 0.1063	0.1097 0.1137	..... .....	{ 0.1097 0.1157 }	..... .....	..... .....	.....	.....	0.1179	0.1179
5.0.....	0.1036	.....	.....	.....	.....	.....	.....	low 0.1127	.....	.....	.....
6.0.....	.....	.....	.....	.....	.....	.....	.....	.....	0.1179	0.1167	.....
.....	0.1067	0.1133	0.1149	.....	{ 0.1109 0.1169 }	..... .....	..... .....	0.1169	.....	.....	.....
8.0.....	..... 73	0.1127	{ 0.1114 0.1149 }	.....	0.1151	.....	.....	0.1141	0.1189	0.1185	.....
9.0.....	..... 0	{ 0.1109 0.1139	.....	.....	.....	.....	.....	.....	.....	.....	.....
10.0.....	..... 0	0.1133	0.1137	.....	{ 0.1120 0.1151 }	.....	.....	0.1189	0.1195	{ 0.1189 0.1207 }	0.1207
11.0.....	..... 0	0.1145	0.1155	.....	0.1163	.....	.....	0.1153	.....	.....	.....
12.0.....	0.1101	0.1145	{ 0.1120 0.1160 }	.....	0.1163	.....	.....	0.1147	0.1207	.....	0.1219
13.0.....	0.1095	{ 0.1140 0.1155 }	0.1155	.....	0.1169	.....	.....	0.1153	.....	.....	.....
14.0.....	0.1060	0.1125	.....	.....	0.1192	.....	.....	.....	.....	.....	.....
15.0.....	0.1095	0.1149	{ 0.1188 0.1171 }	0.1191	{ 0.1199 0.1175 }	0.1208	0.1211	0.1209	0.1223	0.1223	0.1229
16.0.....	.....	{ 0.1125 0.1165 }	.....	.....	.....	.....	.....	.....	.....	.....	.....
17.0.....	.....	{ 0.1125 0.1155 }	0.1188	0.1191	0.1199	0.1202	0.1205	0.1211	0.1212	0.1207	.....
18.0.....	0.1098	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
20.0.....	0.1148	0.1183	{ 0.1193 0.1186 }	0.1191	{ 0.1199 0.1208 }	0.1202	{ 0.1219 0.1217 }	0.1217	0.1212	.....	.....
23.0.....	.....	0.1184	{ 0.1199 0.1186 }	0.1202 0.1209	0.1217 <sup>2</sup>	.....	.....	.....	.....	.....	.....
25.0.....	.....	.....	0.1200	.....	.....	.....	.....	.....	.....	.....	.....
26.0.....	.....	.....	0.1187	.....	.....	.....	.....	.....	.....	.....	.....

<sup>1</sup> From the column headed "20 cc." on, in the majority of cases a 24 per cent. solution was diluted to one-half, the resulting strength being the same as that indicated in the table.

<sup>2</sup> Twenty-eight cc. of tannin used.

NOTE—The figures in ordinary type are those of the regular series in which the nitrogen in the tannin solution used was undetermined. The figures in black-faced type do not belong to the regular series. In all of these cases the nitrogen in the tannin used was determined. The fact that these figures are lower than those of the regular series is due to the allowance made for the nitrogen in the tannin, as well as to the fact that a different lot of tannin was used.



perature was greater in amount than that precipitated at 40° C. Moreover, the lower the temperature, the clearer was the supernatant liquid and the more complete the precipitation. The supernatant liquid in the case of the precipitations made at 40° C. was quite commonly turbid, and in many cases filtration was entirely impracticable. In the case of the precipitations made at room temperature the supernatant liquid, though usually clear, was occasionally turbid and filtration difficult. With the precipitations made in the refrigerator at a temperature of about 12° C. the supernatant liquid was almost always clear and the filtrations (which were also conducted in the refrigerator) rapid and satisfactory, leaving a perfectly clear filtrate.

#### COMPARISON OF VARIOUS TANNINS.

Different samples of tannin do not give uniform results with a given mixture of proteids and meat bases. The difference in some cases is so great as to lead to considerable inaccuracy, and it is of course essential that a uniform tannin be used in the prosecution of any particular investigation. At the same time there has been nothing in our experience to indicate that this difference is so great as to preclude the practicability of comparing in a general way the work of different laboratories. The lack of uniformity is considerable, however, and impairs the value of such a comparison. The results of this study are given in Tables VII and VIII. One important consideration that appears to have been overlooked is the nitrogen content of tannin. As will be seen in Table VIII the amount of nitrogen contained

TABLE VII.—COMPARISON OF THE PRECIPITATING POWER OF TWO TANNINS ON 1 GRAM OF SOMATOSE IN THE PRESENCE OF VARYING AMOUNTS OF SALT.

Tannin solution.	Sodium chloride. Per cent	Nitrogen precipitated. Gram.	Difference in nitrogen precipitated. Gram.
A <sup>1</sup> .....	7	0.1127	
B <sup>2</sup> .....	7	0.1153	0.0026
A.....	10	0.1132	
B.....	10	0.1153	0.0021
A.....	15	0.1143	
B.....	15	0.1169	0.0026
A.....	20	0.1159	
B.....	20	0.1181	0.0022

<sup>1</sup> Nitrogen per 10 cc. = 0.0020 gram.

<sup>2</sup> Nitrogen per 10 cc. = 0.0012 gram.

in some samples of tannin is considerable, and a correction must always be made. A varying amount of the nitrogen in the tannin is either insoluble in water, or is precipitated from a tannin solution by sodium chloride, and hence is insoluble in the tannin salt reagent. It is important that blanks be run with the reagents employed, and that a correction be made for the total nitrogen in the tannin employed as well as the nitrogen in the tannin insoluble in the tannin salt reagent.

In Table VIII are given the results of the influence of reagents prepared from three samples of tannin upon solutions of somatose. In all cases the volume of the liquid in which the precipitation occurred was 100 cc., and contained 2.49 grams of tannin and 10 grams of salt. In the three samples the amount of nitrogen varied from 0.1155 to 0.1191 gram. The nitrogen content of the tannin itself must also be taken into consideration. This is a factor which we have only recently considered in connection with this work, but the amount of nitrogen has been found so great that it should always be determined and a correction applied. The three samples mentioned were found to contain 0.0007 to 0.0052 gram of nitrogen in 20 cc. of the sample.

TABLE VIII.<sup>1</sup>—NITROGEN CONTENT AND COMPARISON OF PRECIPITATING POWER OF VARIOUS TANNINS.

Reagent	Total nitrogen Gram	Nitrogen precipitated Gram <sup>2</sup>	Nitrogen in the 2.49 grams of tannin used Gram
No. 1 Tannin.....	0.1249	0.1191	0.00068
No. 2 Tannin.....	0.1249	0.1165	0.00112
No. 3 Tannin.....	0.1249	0.1155	0.0052
No. 4 Tannin.....	0.1249	.....	0.0104

To further study this question the nitrogen precipitate was obtained on quantities of 1 gram of somatose, using the tannin salt precipitate prepared from two of the above lots of tannin. The results are given in Table VII. In all cases the precipitations occurred in 100 cc. of liquid, which contained 12 grams of tannin and the amount of sodium chloride given in the table. It will be seen that the difference in precipitating power of the two tannins is of considerable magnitude. In all cases in both Tables VII and VIII the quantity of nitrogen contained in the tannin itself

<sup>1</sup> All tannin solutions were made 12 per cent. and 20 cc. used in each case. Ten grams of salt were also added and 1 gram of somatose used. Ice box temperature, 12°.

<sup>2</sup> Corrected for nitrogen content of reagent.



has been allowed for, and is not responsible for the difference shown in the precipitating power of the various tannins.

#### PRESERVATION OF TANNIN SALT REAGENT.

It is well known that tannin undergoes fermentation in solution and loses to a large extent its power of precipitating proteids. We have found that this occurs even in the presence of a considerable quantity of salt, and that the tannin salt reagent should be kept in a cool place, and should not stand more than a few days before using.

#### DETAILED DESCRIPTION OF MODIFIED TANNIN SALT METHOD.

One gram of meat powders, 2 grams of preparations of pasty consistency and from 10 to 20 cc. of liquid or semiliquid extracts should be employed. Solid and pasty preparations are dissolved in a little cold water in a 100 cc. graduated flask, keeping the volume within 20 cc.

Then 50 cc. of a solution containing 30 grams of sodium chloride per 100 cc. are added and the flask agitated to insure the thorough mixing of its contents and the solution of the sample. The flask is now placed in the ice box at approximately  $12^{\circ}\text{C}$ . After the solution has reached the ice box temperature (this requires an hour usually) 30 cc. of a 24 per cent. solution of tannin (which must be at ice box temperature) are added. The total volume is now diluted to 100 cc. The contents of the flask are thoroughly mixed and the flask returned to the ice box, where it remains over night. In the morning the solution is filtered at ice box temperature into a 50 cc graduated flask. The nitrogen is determined in this filtrate, and also in an aliquot portion of the filtrate from a blank, in which the reagents alone are employed. The nitrogen found in the 50 cc. portion multiplied by two (after correction for the nitrogen in the blank) gives the total nitrogen in the filtrate, and includes the nitrogen present as ammonia and all of the nitrogen of the meat bases except that portion of the creatine precipitated by the tannin salt reagent.

In the examination of products that contain insoluble or coagulable proteids, 20 cc. of the filtrate from the coagulable proteids are used for this determination. The volumes of the solution of the meat extract employed, and of the two reagents will then make 100 cc. and require no further dilution. The nitrogen thus precipitated by the tannin salt reagent (calculated

by difference) consists of that present in the form of proteoses and peptones, and the peptone nitrogen may of course be found by deducting the proteose nitrogen, obtained by precipitation with zinc sulphate, from the total amount of nitrogen precipitated by the tannin salt reagent.

#### DETERMINATION OF CREATINE AND CREATININE.

It is stated above that the error occasioned by the precipitation of a portion of the creatine by the tannin salt reagent may be corrected by determining the creatine before the application of the tannin-salt reagent, and in the filtrate from the precipitate given by that reagent. At the suggestion of Prof. L. B. Mendel the method of Folin<sup>1</sup> for the determination of creatine in urine was applied by us to the determination of creatine in meat extracts. Before applying the method it was of course necessary to convert the creatine present into creatinine by dehydrating with hydrochloric acid. As we have noted above, the tannin salt reagent precipitates a portion of the creatine in mixtures of albumoses, peptones and creatine. This is also the case in meat extracts and the proportion of creatine precipitated by the tannin salt reagent varies with each individual extract, as one would suppose. It was therefore necessary to determine the total creatinine (after dehydrating with hydrochloric acid) in the original sample, and also in the peptone filtrate, the difference being the creatine precipitated by the tannin salt reagent. In making the creatine determination on the original sample, a portion of the filtrate from the coagulable and insoluble proteids was employed. The amount used corresponded to about 2 grams of the original solid extract. In the case of the peptone filtrate some trouble was experienced, as the tannin which was present in large quantities interfered and it was necessary to remove it. The following method of procedure was consequently adopted:

From 40 to 50 cc. of the tannin salt filtrate was heated on the steam-bath with hydrochloric acid to convert all creatine to creatinine, 5 cc. of 10 per cent. barium chloride solution were added and sodium hydroxide to distinct alkalinity. The contents of the flask were then thoroughly mixed by shaking, filtered, and the precipitate washed with water. From the filtrate and washings, which are now practically free from tannin, the excess of

<sup>1</sup> Z. Physiol. Chem. 10, 391, 1886.

barium is removed by precipitation with sulphuric acid, filtered, and the precipitate washed. The filtrate is now ready for the usual application of the creatine method. When very small quantities of creatine are present, the usual difficulties of reading are experienced, but in most cases the readings ran from 2 mm. to 12 mm. on the Duboscq colorimeter. The percentage of peptones as determined is corrected by the figure thus obtained. It is of course necessary to determine ammonia in the original sample and make a correction therefore in the calculated percentage of peptones.

### THE PHOSPHORUS CONTENT OF FECES FAT.<sup>1</sup>

BY J. H. LONG AND W. A. JOHNSON.

Received July 13, 1906.

In a recent communication<sup>2</sup> attention was called by one of us to the high phosphorus content of the feces fat of a man in normal health, under conditions where, according to the usual statements in the literature, little or no phosphorus should be found. The phosphorus, in the form of phosphoric acid, obtained from feces fat, as extracted by perfectly dry ether, has always been assumed to have its origin in bodies of the lecithin type, and the detection and estimation of lecithin here have been made to depend on the recognition and determination of phosphoric acid among the products of decomposition of the fat.

However, that all the ether-soluble organic phosphorus obtained through the extraction of dried feces may be assumed to come from a lecithin body may well be doubted, in view of the many conflicting results obtained in the last few years in the examination of fresh animal and vegetable tissues as well as of feces. All the more recent investigations on the subject agree in suggesting that what has been called "lecithin" is evidently a mixture, and as a preliminary to the discussion of the nature of the phosphorus-containing bodies in the feces we have thought it well to make a new series of phosphorus, and also nitrogen determinations in the fat extracted under certain conditions.

In the paper cited above the method of extracting the fat was referred to. In the work below the same plans were followed,

<sup>1</sup> Presented at the June (1906) meeting of the American Chemical Society at Ithaca.

<sup>2</sup> Long: This Journal, 28, 704.

but in one case when a large quantity of the fat was desired, the dried mass was rubbed up with fine crushed quartz and extracted in the Soxhlet apparatus in the usual manner. The ether used in the extractions was carefully purified and finally distilled from sodium. The evaporation of the ether after extraction left a crude fat which was purified by dissolving in dry ether, filtering from a slight residue always left and evaporating again. This treatment would exclude inorganic substances, and anything above a trace of glycerophosphoric acid, if present. The direct ignition of some of the fat thus purified left always a minute amount of residue of phosphate or phosphoric acid. On igniting the fat in the usual manner with sodium or potassium nitrate and carbonate the whole of the phosphorus was left as alkali phosphate which was always determined by the Pemberton method.

The table following gives the results obtained from the feces of seven individuals in normal health living on an ordinary mixed diet. There are also given, in No. 8, the results for nitrogen and phosphorus in the feces of the same man from whom sample No. 3 was obtained at an earlier period.

No. of sample.	Solids	Per cent of fat in dry material.	Per cent. of $P_2O_5$ in fat.	Per cent. of N in fat.	Per cent of P in fat.
1.....	15.03	8.60	1.02	....	....
2.....	24.25	14.01	1.77	....	....
3.....	28.00	19.45	2.32	....	....
4.....	21.99	18.63	1.05	....	....
5.....	20.00	9.50	0.20	....	....
6.....	24.90	14.12	0.80	....	....
7.....	28.00	15.15	1.20	...	....
8.....	....	16.60	3.66	0.47	1.59

Extreme variations are shown in the percentage amounts of phosphoric acid recovered from the fat. As found before, these amounts are not increased by prolonged extraction. It will also be noted that these results are very high in samples Nos. 3 and 8, which, as mentioned, were from the same individual. It should be stated, in addition, that the very high phosphorus content referred to in our earlier paper was found in feces fat from the same man. As yet we have not been able to discover an explanation for this peculiarity.

All the results in the above table are relatively high and if calculated to ordinary lecithin it is plain that the lecithin content of normal human feces must be considered as high instead of

low as frequently stated. Some references to this subject may be found in the excellent book by Schmidt and Strasburger<sup>1</sup> where certain authorities are quoted. It must be remembered that 1 per cent. of phosphorus corresponds to 26 per cent. of distearyl lecithin, or 1 per cent. of  $P_2O_5$  to over 11.3 per cent. of the same complex fat. The relations for the other possible lecithins are not greatly different. On the assumption that this phosphorus content is due to a pure lecithin solely, and that no other soluble nitrogen compounds are present, a check on the phosphorus content would be secured through a determination of the nitrogen. In ordinary distearyl lecithin the nitrogen and phosphorus stand to each other in the ratio 14:31, but the above table shows a phosphorus percentage much higher than this. The discrepancy may be due to the presence of other bodies, containing nitrogen or phosphorus, or both, in the ether extract, or it may be due to variations in the composition of lecithin itself. Wintgen and Keller<sup>2</sup> give some figures for lecithins prepared from soy beans, and purified by acetone precipitation, in which the nitrogen content is relatively high, in some cases 50 per cent. higher than could correspond to a simple formula, while the phosphorus content is low. It is evident that under the name "lecithin" a number of substances are included which may be only remotely related to bodies of the simple distearyl lecithin type, and for the present we can do no better than refer to them as *lecithans* or, less distinctively, as *phosphatides* as suggested by several writers. There is a very considerable literature on the occurrence and nature of these bodies, the extent of which may be gathered from recent papers by Schulze and Winterstein,<sup>3</sup> and Koch and Woods.<sup>4</sup> It may be well to recall that Thudichum,<sup>5</sup> in discussing the organic phosphorus compounds of the brain and other organs of the body, described a number of substances, which he classed as phosphatides, in which the phosphorus and nitrogen ratios were quite variable. Some of these bodies appeared to contain two atoms of phosphorus in the molecule. In other compounds he found a great excess of nitrogen, from which the ratio of N:P appeared

<sup>1</sup> "Die Faeces des Menschen," p. 160.

<sup>2</sup> Abs. Biochemisches Centralblatt, 5, 272 (1906).

<sup>3</sup> Z. physiol. Chem. 40, 101 (1903).

<sup>4</sup> J. Biol. Chem. 1, 203 (1906).

<sup>5</sup> Thudichum; "Die chemische Konstitution des Gehirns des Menschen und der Thiere," Tübingen, 1901.

to be 4:1 instead of 1:1, as in the simple lecithins. Quite recently Winterstein and Hiestand<sup>1</sup> have described a new group of vegetable products which appear to consist of a combination of a lecithin and a carbohydrate. Former investigators had included this with the lecithins of low phosphorus content, but the authors now point out the true relation of these bodies.

However, we are not now concerned with the question of the variation in the composition of these lecithin bodies, but with that of their occurrence in the fat of feces. There can be two general sources for these phosphorus-containing fats. They may represent unchanged substances from the original animal or vegetable foods, or they may represent products of metabolism within the human body. Probably each source contributes a share, but if we consider a large fraction as coming from the food it will be necessary to assume that lecithins are more resistant to the digestive operations than are the other fats since the proportion found in the feces fat is relatively higher. The behavior of the lecithin fats in this respect has been pointed out by Stassano and Billon.<sup>2</sup> Estimating from the phosphorus content about 4 grams daily of lecithin in the feces would be indicated by the maximum of the results in the table above, while the other results are much lower. From a vegetable diet alone it is scarcely possible to account for this largest value, but from a mixed diet containing eggs the difficulty is less. But a large part of the crude fat of the feces is known to have other origin than that of the original food directly. Some comes from the destruction of the tissues lining the intestinal tract, some from the bile and some from the bacteria of the intestine. The importance of the bile in this respect has been generally overlooked, since the older analyses in general placed the organic phosphorus content very low. But the investigations of Hammarsten<sup>3</sup> on the biles of different animals have placed the matter in a new light. Hammarsten shows that a very considerable portion of the alcohol-soluble fraction of the bile solids may be classed in the lecithin or "phosphatide" group. The phosphorated fat found in the bile must have its origin in the

<sup>1</sup> Z. physiol. Chem. 47, 496 (1906).

<sup>2</sup> Jahresbericht über die Fortschritte der Thier-Chemie, 33, 76 (1903).

<sup>3</sup> See, especially, article in the *Ergebnisse der Physiologie*, 4, 1 (1905); "Zur Chemie der Galle."

disintegration of liver tissue, the lecithin content of which is relatively high.

It must be remembered, further, that bacterial cells make up a considerable fraction of the dried feces. Nothing very definite is known of the fat content of the intestinal bacteria, but of certain bacteria from other sources it has been shown that the fat content is high. This is especially true of the tubercle bacillus,<sup>1</sup> but of the minute composition of such fats not much is given in the literature. In view, however, of the general nature of bacterial cells it is fair to assume the presence of lecithin-like bodies in their fat.

Since numerous investigations of recent years have shown the great importance of the lecithins in relation to problems of nutrition, metabolism, and immunity, we have undertaken a continuation of this work with the hope of defining more closely the nature of the phosphorus compounds in the feces fat.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,  
CHICAGO, July, 1906.

## DISCOLORATION OF FRUITS AND VEGETABLES PUT UP IN TIN.

BY F. A. NORTON.

Received July 19, 1906.

A NUMBER of cases of discoloration of fruits and vegetables put up in tin have come to the attention of the writer. In most cases the discoloration was undoubtedly due to sulphides of the heavy metals, the discoloration in some cases being confined to the container, in others affecting the fruits and vegetables as well. The source of the hydrogen sulphide varied in different cases. Some micro-organisms are capable of evolving hydrogen sulphide through breaking down of proteid matter, but this would result only with goods which were not properly sterilized and is not so frequent as some other causes. Also such goods are unfit for consumption so that the discoloration is of minor importance. In other cases hydrogen sulphide resulted from the use of sulphites in connection with fruits, reaction having taken place between the sulphites and vegetable acids with the liberation of sulphurous acid, which, acting upon the tin of the container, had produced

<sup>1</sup> See among other authorities, De Schweinitz: *This Journal*, 25, 354 (1903).

hydrogen sulphide. Another source of hydrogen sulphide was the decomposition of proteid matter through the use of an exceptionally heavy process by the action of steam under pressure on the proteids. Where discoloration had taken place in the goods, the source of the heavy metals was the tin plate and solder of the container.

All fruits and vegetables, as has been shown by Leach,<sup>1</sup> have a greater or less solvent action upon the tin plate and solder of the container, taking up variable amounts of tin and lead, the extremely acid fruits, like rhubarb, being most active, though some of the vegetables, such as squash and pumpkin, take up very large amounts of tin.

Having pointed out the source of the heavy metals and the hydrogen sulphide, one can very readily understand how the discoloration of these goods would take place. A history of some cases in point will best illustrate the different forms of discoloration.

Recently, some badly discolored pears were sent in to the laboratory for examination. On opening the can a heavy brownish black deposit was discovered over the inside of the can, and wherever the pears came in contact with the can there was also the same deposit on the fruit, rendering it unsightly and unfit for the market. Previous experience by the director of the laboratory, Mr. E. W. Duckwall, at once suggested that sulphites had been used in the preparation of the fruit, and that the discoloration was probably due to their use. Determinations for sulphites were made and they were found to be present in very large quantity. The character of the discoloration, which almost assumed the form of a deposit, suggested to us that it was due to metallic sulphides, principally tin sulphide, resulting from the reaction between the sodium sulphite, vegetable acids and tin.

In order to ascertain whether this was the case or not, pieces of pear of good color were placed in two beakers with pieces of tin and solder in each. To one sodium sulphite was then added and the other simply left in water. The pear not treated with sodium sulphite kept its color perfectly on standing in contact with the tin and solder, but the pear in the beaker to which sulphites had been added soon began to darken, and in the course of two or three days the same brownish black appearance observed in the

<sup>1</sup> "Food Inspection and Analysis," p. 696.



discoloration of the pears in the case at hand had permeated nearly the whole pear tissue of the sample under treatment in the beaker. Some of the brownish deposit, also some of the discolored fruit from the can showing the discoloration, was treated with strong hydrochloric acid, which immediately destroyed the discoloration of the pear tissue and brought the deposit into solution. On diluting, filtering and precipitating with hydrogen sulphide, a small quantity of tin sulphide was obtained, which indicated that the discoloration was due to sulphide of tin and other metallic sulphides. This was further confirmed by treating the inside of the discolored can in which the pears had been put up with strong hydrochloric acid, and testing the fumes given off with lead acetate paper for hydrogen sulphide. A very positive reaction was obtained for sulphides, which was confirmed by other tests. In fact, the odor of hydrogen sulphide evolved from the decomposition of the sulphides seemed to be unmistakably present. This experimental data seemed to show conclusively to us that the discoloration was due to metallic sulphides resulting from the hydrogen sulphide which had been liberated by reaction between the sulphites and the tin, aided by the fruit acids present.

To further test this view pieces of tin foil were treated with sodium sulphite and also with sulphurous acid solution. The tin foil in the sulphurous acid solution quickly became discolored with a considerable brown deposit, which was shown to be tin sulphide, while that in the sulphite solution remained perfectly bright. This would indicate that there would not be much danger of discoloration from reaction between sulphites and tin in a neutral medium, but that where sulphurous acid would be liberated discoloration would be very sure to result.

Other pieces of tin foil were then treated in beakers with sodium sulphite solution to which various acids, such as acetic, lactic, tartaric, citric and others, had been added. In each case discoloration resulted, showing that the vegetable acids had liberated sulphurous acid, which in turn reacted with the tin to form tin sulphide, giving the discoloration. Most fruits contain appreciable amounts of such acids as citric and malic acid. In some cases, where fermentation has taken place to any extent, acetic or lactic acid is present, and fruits or vegetables containing any

of these organic acids, if treated with sulphites, are very sure to produce discoloration.

Soldering fluxes sometimes are somewhat acid, and if a little excess is used, permitting the acid to come in contact with the goods, if these are treated with sulphites, discoloration is very sure to be observed at points where the acid has come in contact with the fruit or vegetable. While it would seem that sulphites can be used without any danger of discoloration in neutral substances, there certainly is much danger of discoloration if they are used in products of a somewhat acid character put up in metal containers.

Discoloration from hydrogen sulphide evolved through the employment of a heavy process is illustrated by the following case: In order to secure the proper cooking of the large siftings of peas, which was not readily accomplished in the blancher, the packer had lengthened the process to fifty-five minutes at  $240^{\circ}$ , with the result that this pack of peas contained a very large percentage of cans containing discolored peas, while the smaller siftings of peas given a shorter process were free from the discoloration. An examination of the peas in the containers showed the cans to be very much discolored, the inside of the can being of a brownish-purple color, though there was nothing in the nature of a deposit. The discoloration of the peas was confined more particularly to those around the outer portion of the can and the discoloration did not extend into the peas to any great extent. Some of the more badly discolored peas were separated out and a determination of tin made, which was found to be present in considerable quantity. Also the discoloration, both of the peas and the can, was soluble in strong hydrochloric acid, which would be the case with tin sulphide. Reactions for hydrogen sulphide were obtained from the inside of the can quite readily, both with lead acetate paper and sodium nitroprussiate. This same discoloration of the can is noticeable wherever a heavy process is employed and had previously been found by the writer to react for sulphides, evidently being due to tin sulphide formed through hydrogen sulphide liberated during the processing. There is seldom discoloration of the contents, but in this case it seemed that sufficient hydrogen sulphide had been liberated, together with the tin and lead taken up by the contents of the can, to produce the discoloration. Experiments which have been made

show that when proteid substances are acted upon by steam under pressure ammonia and hydrogen sulphide are split off from the proteid molecule, with the formation of albumose and peptone. Dr. Long, in his recent work<sup>1</sup> in his discussion of proteid substances, gives special attention to the decomposition of proteid substances by steam under pressure, stating that if the temperature is high enough the reaction will extend even beyond the formation of ammonia and hydrogen sulphide, resulting in the complete destruction of the proteid molecule. This would explain the source of the hydrogen sulphide, and, taking into consideration the fact that tin and some lead would have been taken up by the peas, would explain the discoloration of the goods.

In order to assure ourselves that sufficient hydrogen sulphide would be produced under a very heavy process to cause the discoloration, two glass jars were filled with peas and to one 50 mg. of stannous chloride were added, and both were processed at 240° for an hour. The peas in the jar to which the tin chloride had been added showed a very marked brown discoloration, from which the other peas were entirely free, which would confirm our findings in this case.

In some cases, especially in corn, we have encountered a discoloration which was more local in character than in the case of the peas just described. In this case the discoloration was confined almost entirely to the vicinity of the seams and cap. As corn is a very stable product and does not change its position in the can it would appear that the discoloration in this case had come more particularly from the solder or from an excess of flux. It has been shown that where a poor grade of solder containing a large amount of lead is used, the action of the fruit or vegetable juice is greater, more metal being brought into solution. Also if an excess of soldering flux, especially if somewhat acid in character, should remain along the seam, it would result in more of the metal of the container being taken up by the contents of the can at those points, and then on liberation of hydrogen sulphide during the process discoloration would result at these points, while the contents of the can otherwise would be free from discoloration.

From the above, it can be stated that sulphites should not be used with goods of an acid character which are to be put up in tin.

<sup>1</sup> "Physiological Chemistry," p. 74.

Where a heavy process is necessary, care should be exercised to avoid the use of an excess of flux or the use of low-grade solder or tin plate which would tend to increase the amount of heavy metals taken up by the goods. Also the length of the process, in order to avoid evolution of hydrogen sulphide, should be as short as possible, consistent with complete sterilization of the goods.

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### NOTES.

*Note on the Insolubility of Ferric Hydroxide in Ammoniacal Solutions.*—Some years ago difficulty was experienced in this laboratory from the very considerable solubility of ferric hydroxide in an excess of commercial ammonia. It was found, however, that if, after precipitation, the excess of ammonia was expelled by heating upon a steam-bath, the iron was precipitated quantitatively. No experiments were performed at the time to determine the nature of the substance which caused the difficulty, but since it was assumed that similar impurities were likely to be contained by any commercial ammonia, the precaution of precipitating iron with the smallest possible excess of ammonia and of expelling the greater part of this slight excess upon a steam-bath before filtration, has been rigorously followed since the time when the difficulty was first encountered.

The experiments described below were directed to determine, if possible, the extent of this solubility as well as its cause. Solutions of ferric chloride containing about 0.25 gram of iron were precipitated with redistilled laboratory ammonia. In different experiments both hot and cold solutions of the ferric salt were employed, and both a large and a small excess of ammonia. In every case filtration, without suction, was carried out immediately after precipitation. It was considered unnecessary to wash the precipitate. The filtrates were evaporated to small bulk and were then tested for the presence of ferric iron by adding hydrochloric acid (free from iron) and potassium sulphocyanate. Although in every case an extremely slight yellow color was produced, by comparison with standard tubes containing known quantities of iron it was determined that the amount of iron in the filtrate was never as much as one one-hundredth of a milligram.

A repetition of these experiments with commercial ammonia which had not been redistilled gave similar results.

Since it was probable that an excessive amount of amines in the ammonia might influence the solubility of the ferric hydroxide, further experiments were performed in which there was added to the ammonia before precipitation from 1 to 3 grams of the hydrochloride of an amine. The hydrochlorides used were those of methylamine, ethylamine, diethylamine, isoamylamine, ethylenediamine, aniline and phenylhydrazine. As before, in different experiments with the same amine, precipitation was carried out both in hot and in cold solution, and with large quantities of ammonia as well as with a small excess. The filtrates were evaporated to small bulk and tested for ferric iron. In a few cases the filtrate was slightly yellow after evaporation, owing to organic matter, but in these cases the greater part of the color was removed by heating with a considerable quantity of iron-free nitric acid. In the experiments with aniline and phenylhydrazine the oxidizing effect of ferric iron was avoided by nearly neutralizing the ferric solution with ammonia before the addition of the hydrochloride.

The largest quantity of iron found in any one of these filtrates was five one-hundredths of a milligram and in most cases the amount did not exceed one one-hundredth of a milligram. A quantity of precipitate as small as this might well have been mechanically dragged through the filter-paper. At all events the error introduced by the use of an excess of ammonia in precipitating ferric hydroxide is much smaller than the other errors incidental to a quantitative filtration, and the expulsion of the excess of ammonia, at the risk of solution of a portion of the precipitate through hydrolysis of the ammonium salts, should be omitted.

Evidently the solubility of ferric hydroxide in ammonia which was previously observed was caused by the presence of some organic impurity of unusual occurrence in ammonia.

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July 24, 1906.

*A New Qualitative Test for Calcium.*—The difficulty of testing for calcium in the presence of barium and strontium, led the

writer to turn his attention to a test for this metal which would not be answered by barium and strontium.

In this connection the action of potassium ferrocyanide has been tried with surprisingly good results, so good in fact, that it seems almost impossible that the reaction has not been used before, in this connection.

As only one reference could be found to the action of potassium ferrocyanide on calcium compounds,<sup>1</sup> the fear of repetition is braved and the test described, in the hope that it may prove useful.

In separating barium, strontium and calcium, the commonly accepted method seems to be precipitation with ammonium carbonate in ammoniacal solution, solution of the washed precipitate in acetic acid, removal of barium by potassium chromate or bichromate, reprecipitation of strontium and calcium by ammonium carbonate in ammoniacal solution, re-solution of the precipitate in acetic or hydrochloric acid, removal of strontium by ammonium sulphate and finally testing for calcium by addition of ammonium oxalate in ammoniacal solution.

The weak point in this scheme is the danger of traces of barium and strontium remaining in solution, with the well-known effect on the calcium test.

The suggested procedure is the same as the foregoing, up to the point of the re-solution of the precipitate after barium has been removed, (except that acetic acid only should be used).

At this point the solution is divided and calcium sulphate added to one portion to test for strontium.

To the other portion, an equal volume of ammonium chloride is added and a few cubic centimeters of potassium ferrocyanide. The presence of calcium is indicated by the formation of a light yellowish green precipitate.

The sensitiveness of the test has been tried on standard solutions of calcium salts and when applied directly to the calcium solutions was found to indicate 1 part of calcium in 7,000 parts. The ammonium oxalate test was also tried and was found to indicate 1 part in 140,000 parts.

The oxalate test was also applied to a series of standard calcium solutions to which strontium had been added. The strontium was removed by ammonium sulphate as in the first method out-

<sup>1</sup> Prescott and Johnson, 1903, p. 212.

lined. Under these conditions the addition of ammonium oxalate caused no precipitate in solutions more dilute than 1 part in 14,000.

The difference is accounted for by the fact that the ammonium sulphate precipitates out a large amount of calcium with the strontium, and by the fact that calcium oxalate is probably more soluble in ammonium sulphate than in water.

The ferrocyanide test was also tried in the regular scheme of analysis and clearly indicated 1 part in 7,000. This 1 part in 7,000 seems to be the solubility limit of the calcium-potassium ferrocyanide.

Under similar conditions and within the limits of the ferrocyanide test, the volume of the precipitate is about four times as great with ferrocyanide as with oxalate.

It might be added that comparatively fresh solutions of potassium ferrocyanide seem to give the best results.

FRED F. FLANDERS.

STATE COLLEGE OF WASHINGTON,  
PULLMAN, WASH.

*Note on the Coloration of Didymium Glass by Radium Chloride.*—About six-tenths of a gram of radium chloride, 7,000 activity, were sealed in a small tube of didymium glass and allowed to remain six months. The colorless glass acquired an exquisite pink color. Unfortunately on analysis, the glass was found to contain manganese. No variation in the absorption spectrum of the glass was observed after the exposure. No electrical or sparking effects were noted when the tube was opened.

*Note on the Preparation of Rubber Samples for Analysis.*—In the course of construction of the buildings of the College of the City of New York, the writer has had to pass upon a number of items involving large contracts. Among these were rubber and cable insulations. The analysis of rubber and insulating material at best is not attended with satisfaction. To eliminate at least one source of error we desired the sample in a pulverulent condition. This was accomplished by thorough chilling with liquid air and grinding under that refrigerant in an ample agate mortar. The analyses were made by Dr. L. H. Friedburg, of this department.

CHAS. BASKERVILLE.

COLLEGE OF THE CITY OF NEW YORK.

*On the Liberation of Formaldehyde Gas.*—After the article by myself and Mr. West, which appeared in the September number of the Journal, was in press, a paper by Daniel Base appeared (August number of this Journal, page 964) on "Formaldehyde Disinfection and Determination of the Yield of Formaldehyde in Various Methods of Liberating the Gas for the Disinfection of Rooms," in which the process of liberating formaldehyde by means of potassium permanganate has been studied. The results obtained by Base are somewhat different from those given above. The authors of this paper have tried apparatus practically the same as that described by Base, but discarded it as unsatisfactory on account of the large amount of formaldehyde left in the residue, as is indicated by Base's analyses. In fact, unsatisfactory results were obtained in all of the numerous experiments where permanganate alone, either crystal or powdered, was used. The best results with pure permanganate were obtained by the use of a calorimeter bomb as a generator. The permanganate in powdered form was placed in the bomb and by means of an electric appliance the formaldehyde was allowed to drop on the permanganate. The increase in the amount of formaldehyde liberated was undoubtedly due to the heating of the bomb, thus driving off more of the formaldehyde than in an ordinary glass generator. A slight increase in the amount of formaldehyde was likewise obtained by bringing the formaldehyde solution in contact with the permanganate in the bomb under diminished pressure. The percentage of formaldehyde liberated in each case, however, was considerably lower than the percentage obtained by mixing the permanganate with sand.

G. B. FRANKFORDER.

### NEW BOOKS.

LES INDUSTRIES DE LA CONSERVATION DES ALIMENTS. PAR X. ROCQUES.  
Paris: Librairie Gauthier-Villars. 1906. xi + 506 pages, 114 figures,  
15 fr.

This book is of special interest to those who wish to follow the commercial processes of preparing all forms of preserved and canned foods for the market. The author treats of these processes in a clear and comprehensive manner, using well-selected illustrations wherever necessary.

A brief historical sketch is first given, showing the progress of food preservation processes since the 17th century, calling special



attention to the epoch-making discovery in 1804 by Appert of the efficacy of canning, and to the studies of Liebig, Masson, Pasteur and others.

Then follows a general discussion of the causes and effects of decomposition in foods, with a theoretical resumé of the phenomena of putrefaction. Considerable attention is given to preservation by heat and to a practical treatment of the canning industry, the general technique of canning various fruits and vegetables as well as of fish, meats, meat products and milk being given in detail.

Preservation by cold is treated in a separate chapter dealing with the question of cold storage as applied especially to meat, fruits, fish, eggs and dairy products. Preservation by desiccation follows, with commercial methods for the drying of the various foods to which the process is applicable.

The chapter on food preservation by antiseptics is of paramount interest, on account of the increased use in recent years of chemical preservatives in foods. While discussing the relative efficiency of the various commonly used antiseptics, the author unqualifiedly and justly condemns the use of these substances in food, with the possible exception of sulphurous acid in wine, the use of which, under certain restrictions in the wine industry, has in his opinion been justified to some extent by long practice.

The final chapter on the preservation of eggs is fairly complete and timely.

It is to be regretted that the usefulness of the book is restricted by the lack of an alphabetical index. ALBERT E. LEACH.

**THE ELEMENTS OF CHEMICAL ENGINEERING.** By J. A. GROSSMAN, with a preface by SIR WM. RAMSAY. London: Chas. Griffin & Co. Philadelphia: J. B. Lippincott & Co. viii + 152 pp. Price, \$1.50.

So far as it goes this is a good book but it certainly does not contain sufficient to convert the average graduate in chemistry into an engineer. The book describes and figures the technical equivalents of the beaker, flask, condenser, fractioning tube, air-bath, blowpipe, crucible, funnel, mortar and measuring vessel. There are chapters on the steam boiler and other sources of power; on the application of heat; on the materials used; on technical research and the designing of plant.

The first thing a chemical engineer must do is to design, lay out and build his building. Little will be found here to help him.

Then he must put in shafting, pulleys and belts, without help so far as this book is concerned. The treatment given to the subjects chosen is also too brief, sometimes apparently from lack of information, as important types are not even mentioned. The book is characterized by diffuseness; what is wanted is specific information in short crisp sentences. Chemical engineering is a large subject. To get even an elementary treatise within 500-600 8vo pages it will be necessary to make every word count.

It may be somewhat doubtful whether any one person can be found able to write a satisfactory treatise, which had better be the result of coöperation from several well versed in different phases of the subject.

EDWARD HART.

DIE CHEMISCHE REICHSANSTALT VON WILHELM OSTWALD Leipzig  
1906

In this pamphlet of twenty-eight pages, after narrating how the plan of a National Bureau of Chemistry took form, Ostwald explains how university laboratories of chemistry are so well organized for instruction as not to be well fitted for some of the most important kinds of chemical research.

The leaders of chemical science in Germany assumed that the proposed laboratory should provide for research in pure chemistry and in applied chemistry, but the technical chemists desired no such concession in the name to their supposed interests, and the new institution, if established, is to be *die chemische Reichsanstalt*, and not *die chemisch-technische Reichsanstalt*. Four divisions are proposed, one for inorganic chemistry including determinations of atomic weight; a second for analytical chemistry; a third for organic chemistry; and a fourth for physical chemistry. For the foundation of such an institution, chemical manufacturers in Germany are ready to provide considerable sums.

Ostwald mentions the fact that part of the activity of our National Bureau of Standards coincides with that of the proposed *chemische Reichsanstalt*.

EDWARD W. MORLEY.

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## THE IGNITION TEMPERATURES OF HYDROGEN-OXYGEN MIXTURES.

BY K. G. FALK.

Received August 24, 1906.

### HISTORICAL INTRODUCTION.

THE determination of the ignition temperature of detonating gas has formed the subject of a number of experimental investigations.<sup>1</sup> In general, one of two methods was employed. Either the gas was enclosed in a sealed bulb and plunged into a bath of known temperature, or it was passed through a tube which was heated from without to a definite temperature. By means of the former method, V. Meyer, first with Krause and later with Askenasy, found the ignition temperature (absolute) of pure detonating gas to lie between  $791^{\circ}$  and  $879^{\circ}$  (or  $518^{\circ}$ – $606^{\circ}$  C.), whereas Emich obtained a fairly constant result of  $862^{\circ}$  (or  $589^{\circ}$  C.). For mixtures containing an excess of oxygen up to 80.4 per cent., Emich found  $844^{\circ}$ – $881^{\circ}$  (or  $571^{\circ}$ – $608^{\circ}$  C.) and with an excess of hydrogen up to 67.7 per cent.  $848^{\circ}$ – $880^{\circ}$  (or  $575^{\circ}$ – $607^{\circ}$  C.). A number of the values found for the mixture  $2\text{H}_2 + \text{O}_2$  by the use of the second method are as follows:

<sup>1</sup> Mallard et Le Chatelier: *Compt. rend.* 91, 825; *Bull. soc. chim.* 39, 2; Helier: *Ann. chim. phys.* [7] 10, 521; Gautier et Helier: *Compt. rend.* 122, 566; V. Meyer und Krause: *Ann.* 264, 85; V. Meyer und Askenasy: *Ibid.* 269, 49; V. Meyer und Freyer: *Ber.* 25, 622; V. Meyer und Raum: *Ibid.* 28, 2804; Mitscherlich: *Ibid.* 26, 163; Bodenstein: *Z. physik. Chem.* 29, 665; Emrich: *Monatsh.* 21, 1061; and others.

Mallard and Le Chatelier. ....	823°	(or 550° C.)
Bodenstein .....	926°-983°	(or 653°-710° C.)
Mitscherlich .....	947°	(or 674° C.)
V. Meyer and Freyer.....	about 973°	(or 700° C.)
Gautier and Helier.....	1113°	(or 840° C.)
Helier.....	1118°	(or 845° C.)

The results obtained by these methods differ greatly, owing to the uncertain method of heating the gas, to the catalytic action of the walls of the vessel, and to the possibility of some combination taking place before ignition. A more detailed discussion will be gone into later in connection with some new experimental data.

#### THEORY.

With regard to the question of ignition temperatures, Professor Nernst gave me the following suggestions:

"Let us consider a given mass of inflammable gas of uniform temperature, the catalytic action of the containing walls being eliminated, as for example in the manner shown in the experimental portion of this paper. The ignition temperature is defined as the temperature at which the gas would ignite if left entirely to itself for some time.

"The temperature of the gas will rise on account of the heat of reaction. On the other hand, the cooling of the gas will tend to neutralize this rise. Considering unit volume in the interior of the gaseous mass, from the law of mass action, the heat evolved would be

$$Q_1 = qkC_1^{v_1}C_2^{v_2} \dots \dots \dots,$$

while the heat given off by conduction and radiation would be

$$Q_2 = \alpha(T - T_0) + \beta(T - T_0)^4,^1$$

where  $q$  is the heat of reaction,  $k$  the specific reaction-velocity,  $C_1$ ,  $C_2$  the concentrations of the reacting substances,  $T$  the temperature of the gas and  $T_0$  that of the surroundings. For the ignition temperature to be reached  $Q_1 > Q_2$ . If the volume of gas is very large, the particles in the inner portions would not lose an appreciable amount of heat, and the larger the volume the lower would be its ignition temperature. In the latter case, the time required for actual ignition would also be increased. In other words, an inflammable gas of infinitely large volume would ignite spontaneously, independently of the lowness of its initial temperature, although only after a great interval of time. If the

<sup>1</sup> See Nernst: *Physik. Z.* 5, 777 (1904).

gas occupies a finite moderate volume, cooling by conduction and radiation would proceed very rapidly, and consequently the heat of reaction per unit volume must be large in order to cause ignition. If  $Q_1$  is greater than  $Q_2$  by not too small an amount, the temperature of the gas would rise rapidly under these conditions. Consequently the ignition temperature would be higher the smaller the volume of the gas, and also the time required for ignition to take place would be less.

"Without developing these views further, attention may be called to the important fact that  $Q_1$  increases with much greater rapidity than  $Q_2$  with increase in temperature. This leads to the conclusion that with a small mass of gas the ignition temperature increases only slightly with decrease in volume, and that an increase in the initial pressure of the gas, acting evidently in the same manner as increasing the initial volume, would exert only a small influence on the ignition temperature."

The preceding views are confirmed by the experiments to be described in the following pages.

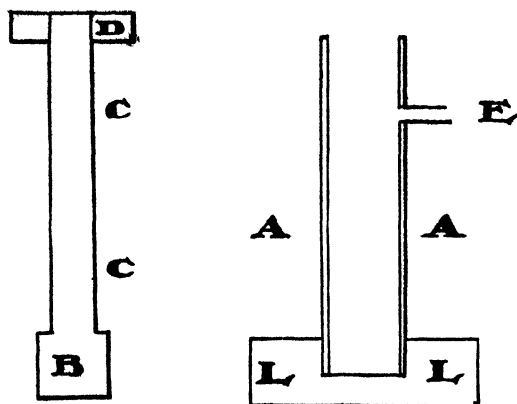
In order to overcome the objections to the methods used heretofore in determining the ignition temperatures of gaseous mixtures, Professor Nernst suggested developing the heat necessary to ignite the gas by the adiabatic compression of the gas itself. This investigation was undertaken to determine the practicability of this method.

#### DESCRIPTION OF APPARATUS.

In order to heat the gas whose ignition temperature was to be determined, it was necessary to enclose it in a small vessel supplied with a device for allowing the gas to be compressed instantaneously. Two pieces of apparatus were constructed on the same plan, but of different sizes.<sup>1</sup> A section vertically through the center is shown in the figure. A steel cylinder, *AA*, was screwed into a wrought iron plate, *LL*, so as to fit absolutely air-tight. The piston head *B* fitted closely into the cylinder *AA*. The piston rod *CC* was made a little narrower (about 2 mm.) than *B*. The piston head together with the piston rod was made of one piece of steel. It was topped by an iron plate, *D*, screwed on to the piston rod. In order to have the piston head slide into the cylinder

<sup>1</sup> I wish to take this opportunity of thanking Mr. Schlüter for his advice and assistance in planning and constructing the apparatus, and Mr. Schlicht for his great aid in carrying out the experiments.

and at the same time permit no leakage, three circular grooves each 1 mm. wide and 1 mm. deep were cut into the former and wound with hemp. The cylinder was filled with the gas to be



studied through *E*, a brass tube 5 mm. in diameter soldered to the cylinder. The compression was obtained after enclosing the gas in the cylinder and pushing the piston down below the opening *E* so as to shut off access to the air by allowing a weight to fall on the plate *D*. By increasing the size of the weight and the distance of its fall, as great a compression, and consequently as high a temperature as was desired, could be obtained. A brass ring, 1 cm. in width, was fitted on the piston rod so that it could be moved up and down only by the use of some force. This served to show the smallest volume of gas in the cylinder during a compression, as the ring was pushed up by the walls of the cylinder as the piston descended, and then remained fixed in position when the piston moved upward again, thus indicating the lowest point reached by the piston. Knowing the dimensions of the apparatus, the volume reached by the compression could then be calculated. Lanoline was found to be the best lubricant for the piston, and was used throughout this work.

The dimensions were as follows:

*Apparatus I.*—Length of cylinder, *AA*, 20.82 cm.; inner diameter of cylinder, 2.50 cm.; thickness of walls of cylinder, 0.51 cm.; distance from lower inner edge of inlet tube to bottom of cylinder, 14.22 cm.; thickness of wrought iron plate, *LL*, 3.24 cm.; thickness of wrought iron plate directly beneath the cylinder, 1.22 cm.; diameter of piston head, 2.50 cm.; length of piston (including



piston head and piston rod), 26.04 cm.; thickness of upper plate, *D*, 2.30 cm. The plate *LL* was firmly bolted to a heavy board.

69.8 cc. gas measured at atmospheric pressure were used in each experiment with this apparatus. To effect the compression a weight of 25 kg. was used, and the height which it was allowed to fall varied from 48 to 86 cm. t 1 1

*Apparatus II.*—Length of cylinder, *AA*, 23.06 cm.; inner diameter of cylinder, 4.40 cm.; thickness of walls of cylinder, 0.73 cm.; distance from lower inner edge of inlet tube to bottom of cylinder, 18.67 cm.; thickness of wrought iron plate, *LL*, 4.95 cm.; thickness of wrought iron plate directly beneath the cylinder, 1.02 cm.; diameter of piston head, 4.40 cm.; length of piston (including piston head and piston rod), 26.25 cm.; thickness of upper plate, *D*, 1.97 cm. The upper plate was fastened by means of two chains to a heavy iron plate on which the apparatus was placed so as to prevent the piston from flying out of the cylinder after an explosion.

283.9 cc. gas measured at atmospheric pressure were used here in each experiment. A 38 kg. weight was dropped a distance varying from 90 to 130 cm.

The following test will serve to show how air-tight apparatus II was. The piston was pushed past the inlet tube, allowed to come to rest, and the distance from the top of the upper plate to the floor measured. A 25 kg. weight was then placed on the upper plate, the air in the cylinder being compressed to a smaller volume. If the piston did not fit in the cylinder so as to be air-tight, the air within, being under pressure, would be forced out between the piston and the cylinder. From time to time the weight was removed and the piston pushed back to its original position by the compressed air within. The distance from the top to the floor was measured each time. In the following table *h* represents these distances and *t* the intervals of time in minutes from the beginning of the test to the successive removals of the weight.

In eight hours the height decreased 1.09 cm. or the volume 16.6 cc. As in the ignition experiments 283.9 cc. gas measured at the ordinary pressure were present. Apparatus I was not quite as tight as this, but it may safely be assumed that there was no escape of gas during the rapid compression which was used to cause ignition.

$h$ (cm).	$t$ (minutes).
39.69	0
39.58	25
39.66	70
39.40	120
39.27	155
39.18	190
38.80	315
38.74	440
38.60	480

In the experiments to be described, only mixtures of hydrogen and oxygen were studied. These were obtained by the electrolysis of a 10 per cent. solution of caustic soda by means of a current having a potential of 110 volts, sufficient resistance being put in the circuit to give a density of about 3 amperes. The electrodes were made of nickel. For the mixture  $2\text{H}_2 + \text{O}_2$  one cell was taken. For mixtures containing more hydrogen or more oxygen, U-tubes were put in series with the first cell, and the gas required taken from the corresponding arm of the U-tube. In this way by using the right number of cells, the following mixtures were obtained:  $4\text{H}_2 + \text{O}_2$ ,  $2\text{H}_2 + \text{O}_2$ ,  $\text{H}_2 + \text{O}_2$ ,  $\text{H}_2 + 2\text{O}_2$ ,  $\text{H}_2 + 4\text{O}_2$ .

The gas was evolved only when required. The glass tubes through which it was necessary to pass the gas were connected by means of thick rubber tubing. In order to have comparable conditions under which to determine the ignition temperatures of the different mixtures, it was decided to saturate the gas in all cases with water vapor at the ordinary temperature. This was done by allowing it to bubble through two or three small wash-bottles filled with water.

#### METHOD OF EXPERIMENTING.

The method of making a determination was as follows: The mixture to be ignited was led into the cylinder by means of a thin rubber tube which passed through the inlet tube, reaching to the bottom of the cylinder. This rubber tube was connected to the glass tube coming from the generating cells right at the edge of the inlet tube. The piston was clamped in position so that the lower edge of the piston head was just above the opening of the inlet tube in the cylinder. In this way the gas was run into the bottom of the cylinder, the displaced air passing out through the inlet tube around the rubber tubing. Owing to the diffusion which was bound to take place the gas was passed in for an hour

before each experiment.<sup>1</sup> After the air had been displaced and the required mixture was present in the cylinder, the rubber tube was withdrawn rapidly, and the piston pushed down past the opening of the inlet tube. The mixture was now confined in the cylinder. The distance from the top of the cylinder to the ground was then measured. This was accomplished in apparatus I by means of a pointer fastened to the plate *D* which marked its height on a blackened plate clamped in position, and in apparatus II by measuring directly the distance from the top of the plate *D* to the upper edge of the lower plate *LL*. Knowing the dimensions of the apparatus, the height  $h_1$  of the volume of gas enclosed in the cylinder was known. The weight was then allowed to fall on the piston, causing a sudden compression of the gas within. The gas was heated in this way to its ignition point, and as soon as this was reached, exploded. The force of the explosion was great enough to stop the downward motion of the piston, even when the kinetic energy supplied by the weight was not entirely exhausted.<sup>2</sup> This was shown most plainly by means of apparatus I with the mixture  $2\text{H}_2 + \text{O}_2$ , where the same results were obtained independently of the height from which the weight fell. From the movable brass ring on the piston rod, already described, the height  $h_2$  of the volume of gas at the moment of explosion was determined. Owing to the high temperature attained by the explosion, some of the lanoline was invariably decomposed. This did not interfere with the determinations as it was only desired to obtain the ignition temperature. There was never any decomposition when no explosion had taken place, although in some cases the ignition temperature was almost reached. The initial temperature of the gas was taken to be that of the room temperature. The initial pressure of the gas was always greater than one atmosphere. Since, in pushing the piston past the inlet tube, the compression began when the piston passed the lower edge of the inlet tube, the distance from this lower edge

<sup>1</sup> A number of experiments in which the gas had been led into the cylinder three to four hours gave no different results.

<sup>2</sup> The terrific force of the explosion can perhaps be better appreciated from the fact that in apparatus I, in an early experiment with the mixture  $2\text{H}_2 + \text{O}_2$ , a piece was blown out of the cast-iron base plate *LL* 0.5 cm. in thickness. The plate was then made of wrought iron and thicker. In apparatus II, where a larger amount of gas was used, the weight (38 kg.) was hurled to a height of 60 to 80 cm. by every explosion.

to the bottom of the cylinder divided by  $h_1$  would be the initial pressure in atmospheres. For apparatus I we have  $14.22/h_1$  and for apparatus II  $18.67/h_1$ .

#### METHOD OF CALCULATING.

In the experiments recorded in the following pages,  $h_1$  represents the initial height in centimeters of the volume of the mixture under examination.

$h_2$ , the final height in centimeters of the volume of the mixture, that is, at the ignition point.

$T_1$ , the initial temperature (absolute) of the mixture.

$T_2$ , the ignition temperature (absolute).

$p_1$ , the initial pressure of the gas in atmospheres.

$p_2$ , the pressure of the gas in atmospheres at the ignition temperature.

$l$ , the distance in centimeters the weight fell (only used with apparatus I for the mixture  $2H_2 + O_2$ ).

The values  $h_1$ ,  $h_2$ ,  $T_1$ , and  $p_1$  were obtained directly from the experiments. To calculate  $T_2$  and  $p_2$  the equation for adiabatic changes

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} \text{ and } \frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^k$$

were made use of.

Since the diameters of the cylinders were constant, by substituting  $h_1$  for  $v_1$  and  $h_2$  for  $v_2$  we have

$$\frac{T_2}{T_1} = \left(\frac{h_1}{h_2}\right)^{k-1} \text{ and } \frac{p_2}{p_1} = \left(\frac{h_1}{h_2}\right)^k.$$

For  $k$ , the ratio of the specific heats of the gases at constant pressure and constant volume, 1.4 was taken. There are no data which define this value accurately under the necessary conditions. The ignition temperatures did not exceed  $600^\circ\text{C}$ . in most cases, and although a small decrease in  $k$  has been observed at this temperature, the increase in pressure in the present experiments may compensate this, as  $k$  increases slightly with the pressure. At any rate, all the determinations are affected equally, and if in future a more exact value for  $k$  is found, the correction of the data here presented would be a simple matter. The equations therefore reduce to

$$\log T_2 = \log T_1 + 0.4 (\log h_1 - \log h_2)$$

and

$$\log p_2 = \log p_1 + 1.4 (\log h_1 - \log h_2).$$

The measurements were made with a steel measuring rod carrying a vernier, so that direct readings to a tenth of a millimeter could be made.

Perhaps the source of greatest inaccuracy lay in the reading of the final height  $h_2$  of the gas. With apparatus I a difference in reading of 0.1 mm. of this height would produce a difference of  $5^\circ$  to  $6^\circ$  in the ignition temperature  $T_2$ , while with apparatus III, 0.1 mm. difference in  $h_2$  would mean  $3^\circ$  difference in  $T_2$ .

## EXPERIMENTAL RESULTS.

The results obtained are shown in the following tables: first for apparatus I for the mixtures:  $4\text{H}_2 + \text{O}_2$ , Table I;  $2\text{H}_2 + \text{O}_2$ , Table II;  $\text{H}_2 + \text{O}_2$ , Table III; and then for apparatus II for the mixtures:  $4\text{H}_2 + \text{O}_2$ , Table IV;  $2\text{H}_2 + \text{O}_2$ , Table V;  $\text{H}_2 + \text{O}_2$ , Table VI;  $\text{H}_2 + 2\text{O}_2$ , Table VII;  $\text{H}_2 + 4\text{O}_2$ , Table VIII.

The average values of  $T_2$  and of  $p_2/p_1$  are also given for each series of determinations.

TABLE I.

		4H <sub>2</sub> + O <sub>2</sub> .		Apparatus I.		
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.)	$T_1$ (abs.)	$T_2$ (abs.).	$p_2/p_1$ .
10.78	0.66	1.32	65.9	293.	896.	49.9
10.48	0.70	1.36	60.0	291.	859.	44.1
8.78	0.52	1.62	84.7	293.	908.	52.3
8.60	0.64	1.65	62.8	294.	831.	38.1
				Average,	874.	46.1

TABLE II.

$2H_2 + O_2$ .		Apparatus I.					
$h_1$ (cm.).	$h_2$ (cm.).	$l$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
8.86	0.74	48.1	1.61	51.9	292.	788.	32.2
8.55	0.59	.....	1.66	70.2	293.	854.	42.3
8.51	0.59	63.2	1.67	70.1	293.	852.	42.0
8.17	0.62	63.2	1.74	64.3	293.	822.	37.0
8.05	0.59	.....	1.77	68.6	293.	833.	38.8
7.74	0.57	67.2	1.84	70.8	290.	823.	38.5
7.60	0.59	52.7	1.87	68.6	292.	809.	36.7
7.24	0.63	63.2	1.96	59.9	293.	778.	30.6
7.12	0.58	.....	2.00	66.8	293.	799.	33.4
6.88	0.54	67.8	2.07	72.9	293.	811.	35.2
6.57	0.56	86.0	2.16	68.0	293.	785.	31.5
6.53	0.46	67.8	2.18	89.3	292.	844.	41.0
6.30	0.55	74.7	2.26	68.5	290.	769.	30.3
6.16	0.56	52.7	2.31	66.3	295.	770.	28.7
5.91	0.44	63.2	2.38	91.7	293.	828.	38.5
4.78	0.38	63.2	2.98	103.0	293.	807.	43.5
Average, 811.							36.3

TABLE III.

$H_2 + O_2$ .		Apparatus I.				
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
10.47	0.86	1.36	44.9	290.	788.	33.0
9.98	0.79	1.43	49.6	290.	800.	34.7
6.54	0.61	2.18	60.2	290.	749.	27.6
6.29	0.49	2.26	80.6	290.	805.	35.7
Average, 786.						32.8

TABLE IV.

$4H_2 + O_2$ .		Apparatus II.				
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
14.91	0.97	1.25	57.4	293.	874.	45.9
14.82	1.00	1.26	54.9	297.	873.	43.6
14.81	0.96	1.26	58.2	294.	878.	46.2
13.45	0.80	1.39	72.2	296.	915.	51.9
12.58	0.75	1.48	76.8	296.	913.	51.9
10.71	0.66	1.74	86.2	296.	902.	49.5
Average, 893.						48.2

TABLE V.

$2H_2 + O_2$ .		Apparatus II.				
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
15.07	1.24	1.24	40.9	293.	796.	33.0
15.06	1.17	1.24	44.3	292.	811.	35.7
15.04	1.06	1.24	50.9	293.	847.	41.0
15.03	1.08	1.24	49.6	293.	840.	40.0
14.71	1.16	1.27	44.5	293.	809.	35.0
14.67	1.11	1.27	47.2	293.	823.	37.2
14.22	1.02	1.31	52.5	293.	841.	40.1
13.83	1.10	1.35	46.7	293.	807.	34.6
13.74	1.06	1.36	49.1	293.	817.	36.1
12.65	1.01	1.47	50.8	293.	805.	34.6
12.30	0.91	1.51	58.1	291.	825.	38.5
12.18	0.92	1.53	57.0	293.	823.	37.3
11.57	0.89	1.61	58.5	291.	812.	36.3
9.31	0.70	2.01	75.1	292.	822.	37.4
Average, 819.						36.9

TABLE VI.

$H_2 + O_2$ .		Apparatus II.				
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
14.98	1.24	1.25	40.8	295.	799.	32.6
14.95	1.28	1.25	39.0	296.	791.	31.2
14.38	1.24	1.30	40.1	296.	789.	30.9
13.91	1.17	1.34	43.0	296.	797.	32.1
13.66	1.21	1.37	40.7	298.	786.	29.7
13.41	1.12	1.39	45.0	296.	799.	32.4
11.95	0.97	1.56	52.6	296.	808.	33.7
Average, 796.						31.8

TABLE VII.

$H_2 + 2O_2$ . Apparatus II.						
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
14.32	1.16	1.30	44.0	296.	809.	33.9
14.16	1.15	1.32	44.3	299.	816.	33.6
13.84	1.19	1.35	41.9	299.	798.	31.0
13.17	1.06	1.42	48.3	294.	806.	34.0
13.09	1.05	1.42	48.8	296.	812.	34.4
12.69	1.05	1.47	48.2	296.	802.	32.8
12.11	1.00	1.54	50.6	296.	803.	32.8
11.81	0.93	1.58	55.5	296.	818.	35.1
Average, 808.						33.5

TABLE VIII.

$H_2 + 4O_2$ . Apparatus II.						
$h_1$ (cm.).	$h_2$ (cm.).	$p_1$ (atm.).	$p_2$ (atm.).	$T_1$ (abs.).	$T_2$ (abs.).	$p_2/p_1$ .
15.05	1.09	1.24	49.0	296.	846.	39.5
13.83	1.00	1.35	53.4	296.	848.	39.6
13.63	0.98	1.37	54.6	296.	848.	39.9
12.79	0.93	1.46	57.3	296.	845.	39.3
12.43	0.87	1.50	60.8	296.	858.	40.5
Average, 849.						39.8

Whether the rise in temperature produced by the adiabatic compression is the only source of heat entering into question in these experiments may be answered affirmatively. The compression is so rapid that there is no chance for radiation to the walls of the vessel. There is no heat developed by friction which could affect the mixture, for even if the sliding of the piston in the cylinder would produce such heat, it would not be in contact with the enclosed volume of gas.

## DISCUSSION OF RESULTS.

The ignition temperatures (absolute) obtained for the different mixtures are as follows:

	Apparatus I.	Apparatus II.
$4H_2 + O_2$ .....	874.	893.
$2H_2 + O_2$ .....	811.	819.
$H_2 + O_2$ .....	786.	796.
$H_2 + 2O_2$ .....		808.
$H_2 + 4O_2$ .....		849.

The pressures at which these temperatures were determined were all greater than 39 atmospheres. It is evident from the tables that differences in pressure over 39 atmospheres produce no appreciable difference in the ignition temperatures.

The effect of the initial temperatures on the inflammability is of great interest. Direct experimental values for the ignition temperatures of the different mixtures when the initial temperatures were higher than the room temperature could not be obtained, because the lanoline used to insure the tightness of the apparatus as well as to act as lubricant, melted, thus permitting leakage between the piston and the cylinder. No other lubricant could be found to answer the purpose at these higher temperatures.

A little consideration will show, however, that the effect of changing the initial temperature is included in the data given. Let us take the state of affairs in an experiment at the instant when the piston in descending reaches a point half way between the starting point and the bottom of the cylinder. At this moment  $h_2 = \frac{1}{2} h_1$  and

$$\begin{aligned}\log T_2 &= \log T_1 + 0.4 (\log h_1 - \log \tfrac{1}{2} h_1) \\ &= \log T_1 + 0.12041.\end{aligned}$$

If  $T_1 = 290^\circ$ ,  $T_2$  would be equal to  $383^\circ$ .

We can now consider this value of  $T_2$  as the initial temperature of the mixture, which, on being further adiabatically compressed, explodes when the ignition temperature is reached. This is evidently the same ignition temperature which was found when the experiment was considered as starting from the room temperature. This method of treating the problem is permissible since the only other factor which changes during an experiment is the pressure and this, as we have seen, does not influence the ignition temperature under the given conditions. In a similar manner, by dividing a single experiment into an infinite number of separate ones in which  $T_1$  (the initial temperature) is successively increased by a small amount, the initial temperatures of all the mixtures can be considered to be varied from the ordinary up to the ignition temperature.

We can sum up briefly by stating that, from the experimental results obtained, the ignition temperature is independent of the final pressure of the gas for pressures greater than 39 atmospheres (this was the least pressure at which the ignition temperature was determined; this constancy probably extends to pressures much less than this), and that the ignition temperature under the conditions described is entirely independent of the initial temperature of the gas. It must be borne in mind that the values for  $p_2/p_1$



do change, depending on the initial temperatures. Those given in the tables refer simply to the cases in which the gas was at the room temperature when  $p_1$  was measured.

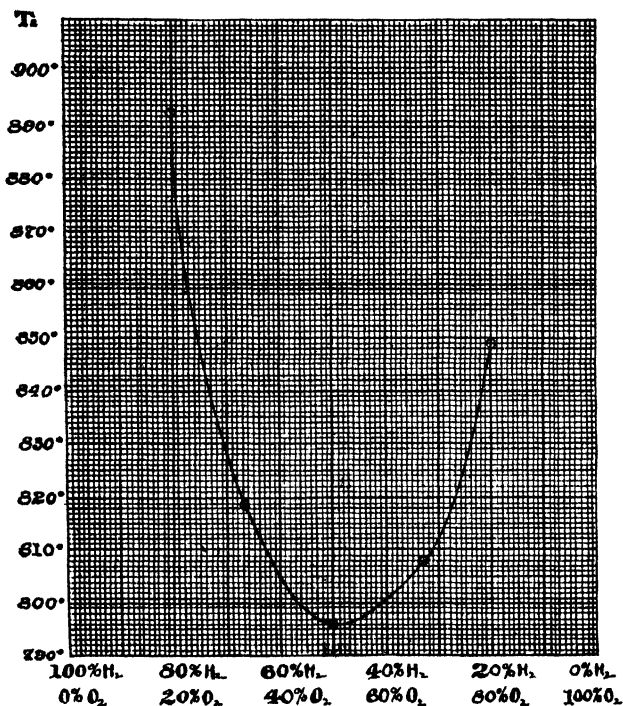
Considering the difference in size between apparatus I and II the agreement in the ignition temperatures is as close as could be expected. Perhaps the values obtained by means of apparatus II are the more accurate, as here a larger volume of gas was used, and the errors arising from the measurements play a smaller part. The discussion of the results will therefore be limited to the experimental values obtained with this apparatus.

The ignition temperature of the mixture  $H_2 + O_2$  lies lower than that of any of the other mixtures studied. This minimum in temperature, corresponding to a maximum affinity, is shown most clearly by means of the accompanying curve in which the relative volumes of hydrogen and oxygen in the different mixtures are plotted as abscissae and the temperatures of ignition as ordinates. The most evident explanation for this is, that in the combination of hydrogen and oxygen, the first product formed is hydrogen peroxide which may or may not be then decomposed, the conditions determining how complete this second reaction is. This theory is not new but up to the present has lacked experimental verification. It was first put forward by Mendeléeff:<sup>1</sup> "...it may be admitted that, in the combination of hydrogen with oxygen, hydrogen peroxide is first formed (equal volumes of hydrogen and oxygen) which is decomposed by the heat evolved into water and oxygen. This explains the presence of traces of hydrogen peroxide in almost all cases of the combustion or oxidation of hydrogenous substances, for it cannot be supposed that water is first formed and then the peroxide of hydrogen, because up to now such a reaction has not been observed, while the formation of  $H_2O$  from  $H_2O_2$  is very easily reproduced." The

<sup>1</sup> This extract is from "The Principles of Chemistry," by Mendeléeff, the English translation of the sixth Russian edition, Vol. I, page 312. The foot-note on the same page states: "This opinion which I have always held (since the first editions of this work), as to the primary origin of hydrogen peroxide and of the formation of water by means of its decomposition, has in later days become more generally accepted, thanks more especially to the work of Traube . . . perhaps the theory of the explosion of detonating gas itself and of the combustion of hydrogen will gain in clearness and truth, and we take into consideration the preliminary formation of hydrogen peroxide and its decomposition."

experimental work of Traube<sup>1</sup> and more recently that of Engler<sup>2</sup> have done much to forward this view.

Emich<sup>3</sup> in an article published in 1897 described a series of experiments in which he determined the length of spark (by measuring the distance between two electrodes) which would just ignite mixtures containing varying amounts of hydrogen and oxygen. He found the greatest inflammability (the inflammability varying inversely as the spark length) with the mixture containing equal volumes of hydrogen and oxygen. On diluting this mixture with hydrogen and then with oxygen, he found that twice as much oxygen was required to cause the same increase in



spark length as hydrogen, or that beginning with the mixture of greatest inflammability— $H_2 + O_2$ —and adding equal volumes first of oxygen and then of hydrogen, the inflammability of the resulting mixture was decreased twice as much by the hydrogen

<sup>1</sup> Traube: Ber. 15, 657; 16, 1201; 18, 1881; 22, 1496; 26, 1471.

<sup>2</sup> Engler and Weissberg: "Vorgänge der Autoxydation."

<sup>3</sup> Emich: Monatsh. 18, 6.

as by the oxygen. As will be seen from the figures on page 1527, the same result was obtained in this work, the ignition temperature being increased approximately twice as much by the addition of hydrogen as by the addition of the same volume of oxygen, beginning with the mixture having the lowest ignition temperature— $\text{H}_2\text{O}_2$ . Emich speaks of the probability of the primary formation of hydrogen peroxide, but in a second paper<sup>1</sup> he appears to have abandoned this view as the result of having determined directly the ignition temperatures of the different mixtures by enclosing them in sealed bulbs and plunging them into baths of known temperature. He found very little difference in the ignition temperatures of the mixtures and concluded that there was no simple relation between this temperature and the thickness of the gaseous layer which could just be ignited by a spark. Mention may be made of some of the other relations found by Emich. The presence of moisture had no influence on the spark length necessary for ignition. When inert gases such as nitrogen or carbon dioxide were added, the inflammability depended solely upon the partial pressures of the hydrogen and the oxygen present.

The work here described shows that ignition temperature and inflammability as measured by Emich do bear a simple relation to each other, and are in fact inversely proportional.

In comparing the results by the method described in this paper with the results obtained by other methods, the ignition temperature of detonating gas only can be discussed. The temperature found in this work is  $819^\circ$ . V. Meyer and co-workers found it to lie between  $791^\circ$  and  $879^\circ$  while Emich found  $862^\circ$  by enclosing the gas in sealed vessels and plunging them into baths of known temperature. Here evidently the whole mass of gas was not heated to the ignition temperature simultaneously. The heat passing through the walls of the vessel would cause catalytic action on the inner surface first, and in the time which, although perhaps very short, it would take the whole mass of gas to reach the required temperature, a certain amount of combination would have taken place. The water which is formed in this way, diffusing into the interior, might also affect the reaction. The pressure in the vessel would be diminished, perhaps below atmospheric pressure, the expansion due to the heating acting in the opposite direction. From the theory of the ignition temperature

<sup>1</sup> Emich: *Monatsh.* 21, 1061.

developed by Professor Nernst, decrease in pressure would mean a slightly higher ignition temperature. Here we have a considerably higher ignition temperature. The amount of combination before ignition in these experiments is very indefinite, and the condition of the gas at the moment of explosion is entirely undetermined.

With regard to the ignition temperature as determined by passing the gas through a tube heated to a known temperature, Mallard and LeChatelier found an average of  $823^{\circ}$ . Other investigators obtained much higher values than this, due doubtless to the fact that the gas did not reach the temperature of the tube when less heat was employed in their determinations. Catalytic action and combination before ignition must act in these experiments as well, while the gas would be under atmospheric pressure all the time. The result found agrees very well with the result obtained here, a slightly higher temperature being found as the theory requires. It is surprising that the catalytic action of the walls has so slight an influence on the ignition temperature.

From the theoretical considerations, these ignition temperatures apply only to moderate volumes of gas, such as are generally worked with in the laboratory. With very minute or very large volumes, other conditions obtain, as shown in the theoretical portion of this paper.

#### THE EXPLOSION WAVE

In order to produce an explosion wave, a gaseous mixture must be heated to a definite temperature, a constant velocity of propagation of the chemical reaction being then attained. In the explosion wave this temperature results from the progressive adiabatic compression of the gas, the velocity of the wave being constant when a certain compression and, consequently a certain temperature, is reached.<sup>1</sup> The absolute final compression for any gaseous mixture need not be a constant; only the ratio of the final to the initial pressures should be.

<sup>1</sup> This theory of the explosion wave was first put forward by Mallard and Le Chatelier; *Recherches expérimentales et théoriques sur la combustion des mélanges gazeux et explosives*, Ann. mines—September to December, 1883. Recently the fact that the explosion wave is purely a hydrodynamical phenomenon has been clearly set forth by Nernst: "Physikalischchemische Betrachtungen über den Verbrennungsprozess in den Gasmotoren," pages 21-31.

In the work described in this paper, the ignition temperatures were reached by adiabatic compression. We have practically the phenomenon of the explosion wave in this compression, chemical action being produced by the rise in temperature brought about by adiabatic compression. We should then expect  $p_2/p_1$  to be constant for any mixture. This is found to be approximately the case from the tables on pages 19-22. The average values for  $p_2/p_1$  are given here.

	Apparatus I.	Apparatus II.
$4\text{H}_2 + \text{O}_2$ .....	46.1	48.2
$2\text{H}_2 + \text{O}_2$ .....	36.3	36.9
$\text{H}_2 + \text{O}_2$ .....	32.8	31.8
$\text{H}_2 + 2\text{O}_2$ .....		33.5
$\text{H}_2 + 4\text{O}_2$ .....		39.8

The mathematical theory of the explosion wave has been worked out by E. Jouquet in very complete form.<sup>1</sup> It is impossible to give even a general account of this interesting work here. His calculations of the velocity of the explosion wave for a number of reactions agree remarkably closely with the values found by Berthelot and by Dixon, especially when the approximate nature of some of the data which he was forced to use is taken into account. He also shows just how near the formulas of Berthelot and of Dixon for calculating these velocities approach the true ones, and why the results calculated from these agree in many cases with the experimental values.<sup>2</sup>

Some of the calculations of Jouquet may perhaps be applied directly to the results here obtained.<sup>3</sup> He puts forward two hypotheses with regard to the actual combination of the gases in the mixtures: first, "la combustion est nulle dans la quasi-onde de choc," and secondly; "cette combustion est notable." Not to enter into details, it may be stated that for the mixture  $2\text{H}_2 + \text{O}_2$ ,  $p_2/p_1$  would be equal to 34.29 in the former case, and to 17.15 in the latter. Jouquet states expressly that this is true only after the wave has been set up and is moving with constant velocity, and not during the period of its formation. Perhaps he referred to the usual manner of setting up an explosion wave by slow preliminary combustion, and not to the method here described. At

<sup>1</sup> E. Jouquet: "Sur la propagation des réactions chimiques dans les gaz," J. mathémat. 1905, 347, and 1906, 5.

<sup>2</sup> Second paper, page 76.

<sup>3</sup> Second paper, page 80.

any rate the value found experimentally is 36.6 which is very close to the value deduced by Jouquet from the first hypothesis.

In conclusion, I wish to express my thanks to Professor Nernst at whose suggestion this investigation was undertaken, for his interest and encouragement throughout the course of the work.

BERLIN, August, 1906.

## THE POLARIZATION CAPACITY OF IRON AND ITS BEARING ON PASSIVITY.<sup>1</sup>

BY C. MCCHEYNE GORDON AND FRIEND E. CLARK

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THIS paper contains an account of some measurements of the polarization capacities of iron electrodes. It was expected that a comparison of the capacity values in a number of different solutions would give some evidence for or against the oxide film explanation of passivity. As will be set forth below, the results found lead us to the conclusion that the oxide film theory is after all the correct explanation.

Finkelstein<sup>2</sup> measured the polarization capacity of iron in concentrated nitric acid by the same method that we have employed, with the same end in view, but came to the opposite conclusion. On the whole his capacity measurements, however, were not necessarily in conflict with the film theory, his main reasons for rejecting this theory being based on his measurements of the potentials of iron.

The method is that first used by Gordon,<sup>3</sup> at the suggestion of Nernst,<sup>4</sup> and later by Scott<sup>5</sup> and others in Nernst's laboratory. It is a comparison of the electrode capacity with that of a metallic condenser in the Wheatstone bridge, with a telephone receiver as the zero instrument. In most cases the method gives a sharp telephone minimum only for small measuring currents, near the limit of audibility of the telephone. In series with the metallic condenser it is necessary to have a variable resistance, in order to balance the resistance of the electrolyte, which is in series

<sup>1</sup> Presented in abstract at the Ithaca Meeting of the American Chemical Society.

<sup>2</sup> Z. physik. Chem. 39, 91 (1902).

<sup>3</sup> Gordon: Z. Elektrochem. 3, 153 (1896); Wied. Ann. 61, 1 (1897).

<sup>4</sup> Nernst: Z. physik. Chem. 14, 622 (1894).

<sup>5</sup> Scott: Wied. Ann. 67, 388 (1899).

with the capacity of the electrodes. In some cases it is necessary to have a resistance also in parallel with the metal condenser, as a balance for the conductance in parallel with the electrode capacity; with some electrodes this parallel resistance is unnecessary. In the interpretation of the results of this paper, this parallel resistance is of special importance.

It has always been considered that the capacities given by this method may be either real electrostatic capacities, due to a high resisting film on the electrode, or only apparent capacities due to the changing of the electrode potential, resulting from concentration changes either in the solutions or electrodes. Aluminium, previously subjected to anodic polarization, affords a typical example of the first case, while mercury and platinum have been regarded as giving capacities due to concentration changes. The latter metals do not require any resistance parallel to the condenser, while the former *generally* does.

However, a good telephone minimum without a parallel resistance does not necessarily mean that there is no high resisting film on the electrode. It may mean, just as well, that the resistance of the film is so high in comparison with the capacity that it has no appreciable effect on the telephone current. We have an example of this in the case of anodic films formed on aluminium; for the thinner films a parallel resistance is necessary, but for the thicker films the resistance is relatively so high as to have no noticeable effect on the telephone minimum. Thus, while the necessity for the parallel resistance can be explained only by the assumption of a high resistance film, its absence may denote either a film of still greater resistance, or, that the capacity measured is not due to a film at all, but to concentration changes.

The electrodes used were iron wires, about 0.8 mm. in diameter, prepared for standardizing work, and marked 99.6 per cent. pure. They were immersed in the various solutions to different depths. In most cases about 0.3 sq. cm. was covered by the solution. The values of capacities and parallel resistances given below are all reduced to values per square centimeter on a single electrode. On account of the action of certain solutions on the iron, the actual size of the surface of some of the electrodes is somewhat uncertain, so that the absolute values cannot be regarded as of great accuracy. The relative values for any pair of

electrodes in different solutions generally agreed within a few per cent.

#### OBSERVATIONS.

*Nitric Acid, Sp. Gr. 1.42.*—In nitric acid, of the above concentration, five pairs of electrodes with surface areas varying from 0.12 sq. cm. to 0.3 sq. cm., gave capacities ranging from 58.7 to 66.0 Mf.; mean, 63.6 Mf.

This is in good agreement with the measurements of Finkelstein. His range of values is somewhat larger, but most of his results come within the above limits. Our observations differ from his in regard to the parallel resistance. He found no evidence of conductivity in parallel with the capacity and considered this partial proof against the so-called film theory. With electrodes as large as those used by Finkelstein, namely, 0.33 sq. cm. or more, we likewise found no improvement of the minimum on the addition of parallel resistance. However, with smaller electrodes (less than 0.2 sq. cm.) a parallel resistance always made the minimum much sharper. The amount of this resistance could not be determined very accurately. The resistance which was evidently too small differed from that evidently too large by about 20 to 25 per cent. Taking the mean of these two observed values, we found for electrodes 0.12 sq. cm. in diameter, in one case, 36 ohms per sq. cm.; and in another, 30 ohms per sq. cm. Electrodes 0.2 sq. cm. gave a resistance of 60 ohms.

That we must have a parallel resistance for the smaller electrodes and not for the larger is, we presume, due to the greater density of the measuring currents with the smaller electrodes. Higher polarization probably reduces the resistance of the films; at all events, it brings their conductance into evidence. The higher resistance found for the larger electrodes indicates that the conductance increases with increased polarization of the measuring current. We take it that with the electrode larger than 0.3 sq. cm., the density of the measuring current being smaller, the parallel conductance was so high as to have no effect on the telephone current. Direct tests on the effect of varying the strength of the measuring current on a single pair of electrodes, as well as measurements of the capacity during polarization by a direct current, will probably give us more information in regard



to the variations of this parallel resistance. Such experiments have not yet been made.

The capacity in fuming nitric acid was about the same as in nitric acid of specific gravity 1.42.

*Dilute Nitric Acid.*—Electrodes which had been made passive in concentrated nitric acid gave in dilute nitric acid, immediately after transference, the same capacity as in the concentrated acid. The capacity remained the same for a greater or less length of time, depending upon how long the iron had previously been in the concentrated acid. After a time, the capacity began to increase quite rapidly, going in less than one minute from the value for the concentrated acid to a pure resistance minimum, without any sign of capacity or polarization. *At the same time the dissolving of the iron in the nitric acid made itself evident.*

Before the increase of the capacity is noticeable, there is a decrease in the sharpness of the minimum, just exactly as would be the case if we had a film whose resistance decreased considerably before its thickness had suffered any appreciable change.

*Ferrous Sulphate.*—Immediately after transference from concentrated nitric acid, we found 58.7 Mf.; after standing ten minutes in the aqueous solution of ferrous sulphate, measurements showed 103 Mf. and 10 ohms. After transference from dilute nitric acid, 80 Mf. and 44 ohms.

After cathodic polarization, with the electrolytic precipitation of iron, there was a sharp resistance minimum without any sign of capacity. After anodic polarization at three volts, the following data were obtained: 120 Mf. and 8.6 ohms.

*Ferric Chloride.*—The capacity was so large in comparison with the parallel resistance that the latter determined, to a large extent, the position of the bridge minimum. The condenser improved the sharpness of the minimum but no reliable measurements of the capacity could be made. After cathodic polarization there was a sharp resistance minimum without the condenser. No signs of a minimum could be obtained with the condenser.

*Hydrochloric Acid.*—Electrode direct from air gave 240 Mf. and 4 ohms. Twenty minutes later, about 500 Mf. and 2 ohms.

The capacity soon became so large in comparison with the

parallel resistance, that no reliable value could be obtained. The minimum was always better with the condenser than without it.

*Sulphuric Acid.*—In concentrated sulphuric acid a sharp minimum was not obtained. Approximate measurements gave 12 Mf. and 24 ohms.

In dilute sulphuric acid, one minute after transference from concentrated nitric acid, we found 136 Mf. and 3 ohms; five minutes later, 186 Mf. and 2 ohms; thirty minutes later, more than 400 Mf.

The parallel resistance was too small for accurate measurements. Electrodes directly from air gave 120 Mf. and 2 ohms. One minute after oxidation in Bunsen flame, 108 Mf. and 2 ohms; and after standing thirty minutes, about 200 Mf., resistance uncertain.

*Sodium Sulphate.*—The iron wire was made passive in concentrated nitric acid, transferred to the sodium sulphate solution and the following measurement recorded, 60 Mf. After fifteen minutes, 110 Mf. to 114 Mf.

After standing in dilute nitric acid for a time, and then transferring to the sodium sulphate, the capacity was at first very large but decreased too rapidly for us to follow with measurements. Finally it came to a nearly constant value at 113 Mf. and 4.7 ohms. After oxidation in Bunsen flame, 13 Mf. and 75 ohms.

When the electrodes were placed in the solution directly from air, the capacity was relatively small, but soon came to a constant at 110 Mf. and 9 ohms.

*Potassium Nitrate.*—Measurements were made in dilute potassium nitrate solution, after the iron electrodes were made passive in concentrated nitric acid, 62 Mf.; and after five minutes, 156 Mf. and 2 ohms.

Five minutes after transference from dilute acid to the potassium nitrate solution, these measurements were taken, 150 Mf. and 3.5 ohms. These values remained constant for forty-five minutes, when the observations ceased.

Taken from air and after one minute measured in the above electrolyte, the following was found, about 6 Mf.; and after five minutes, 14.4 Mf.; after four hours, 118 Mf. and 12.5 ohms. After

oxidation in Bunsen flame, the first trial gave 3 Mf.; the second trial, 25 Mf. and 14 ohms. After two hours' anodic polarization of 0.5 volt, 76 Mf. and 11.00 ohms. After same polarization for twenty-four hours, 61.6 Mf. and 15.0 ohms. Thus by long-continued polarization the capacity was brought to the same value as in concentrated nitric acid.

*Sodium Hydroxide.*—With electrodes from the air, the minimum was so poor that no measurements were made. After anodic polarization of 1.5 volts for five minutes, we got 43.6 Mf. and 4.7 ohms. The polarization was continued for two hours and the capacity and resistance found to remain constant. Cathodic polarization made the capacity too large for the taking of accurate measurements, but not large enough to take resistance measurements without a condenser. After oxidation in a Bunsen flame, we found 3 to 4 Mf. and 30 ohms.

#### DISCUSSION.

The measurements show that, in general, the polarization of iron electrodes can be balanced by a condenser, *with a resistance in parallel*. Only four exceptions to this were found, in dilute nitric acid and in ferrous sulphate and ferric chloride after cathodic polarization, the iron behaved as a non-polarizable electrode; with the larger electrodes in concentrated nitric acid, the parallel resistance was not necessary.

We found the parallel resistance necessary, however, with the smaller electrodes in concentrated nitric acid, and the smaller the electrode, the less the resistance per square centimeter. We conclude that failure of the method to give evidence of parallel conductivity in the case of large electrodes was due to the conductance being so small as to have no appreciable effect on the telephone current. *Since the resistance in parallel with the condenser can only be interpreted as being due to a poorly conducting film, we hold that our results present very strong evidence in favor of the film theory.*

Probably the most surprising thing in connection with the results, is that in neutral and acid solutions, where iron is active, we found the capacity of the same order of magnitude as in the concentrated nitric acid. In the latter the capacity is about 60 microfarads while in sodium sulphate, after treatment with dilute nitric acid, as well as after being made passive in concen-

trated nitric acid, the capacity soon came to about 110 microfarads. In dilute sulphuric acid, soon after immersion from air, with gas bubbles being evolved on the iron, the capacity was only 160 microfarads. The difference between active and passive iron is not shown so much in the magnitude of the capacity as in that of the parallel resistance. It seems that in most solutions iron is covered with an oxide film, comparable in thickness with that formed in concentrated nitric acid, but in the latter electrolyte its resistance is much greater.

Our results are, in most respects, a confirmation of the views on the question of passivity lately expressed by Haber and Goldschmidt,<sup>1</sup> whose paper came to our notice after the greater number of the above measurements had been completed. They have shown that the assumption of an oxide film, not perfectly continuous, but full of pores, and the presence of such a film in solutions where iron is only partially passive, does away with most of the objections to the film theory of passivity. The pores, assumed by them, readily explain the parallel conductivity, which we have found. It is not necessary to assume metallic conduction for the film to account for the results of Finkelstein, as we have shown that his measurements are not contradictory to the idea of a film of high resistance. The greater conductance found by us for larger densities of measuring current, we conceive as being due to an enlargement of the pores, although the formation of higher oxide threads with metallic conduction would also explain the phenomena.

Apparently the strongest argument against the film theory is that due to the observations of Müller and Königsberger,<sup>2</sup> who found no difference in the reflecting power of active and passive iron. Our results confirm the supposition of Haber and Goldschmidt, who infer that Müller and Königsberger were measuring the reflecting power of an oxide film in all cases, and naturally found it the same.

Finkelstein sees in the fact that the capacity of iron in concentrated nitric acid is near that of platinum (bright), after it has been heated in a flame, an argument against the film theory and in favor of the idea that the capacity is due to concentration changes, which has heretofore been considered the case with gold

<sup>1</sup> Z. Elektrochem. 12, 49 (1906).

<sup>2</sup> Physik. Z. 5, 413, 797 (1904); 6, 847 (1905).

and platinum. We consider it more probable, in view of the still larger capacities which we have found with parallel conductance, and in view of the fact that Scott found the capacity for gold (10.3 *Mf. sq. cm.*) almost the same as that for aluminium (10.6 *Mf. sq. cm.*), where there certainly is such a film, that gold and platinum, likewise, are covered with an oxide film, which is at least the main factor in determining their capacity. From the very irregular values of capacities found for platinum, except after it has been heated in the flame, it appears as if such heating produces a very regular film, which slowly changes when left standing in air or in solution.

The capacity of platinized platinum is many times larger, but it is not at all improbable that here, too, the size of the capacity is largely determined by such a film. By this assumption a number of facts can be explained, which are hard to reconcile with the heretofore accepted theory that the capacity is due to changes in concentration of gas occluded in the electrode. A few of these facts we shall merely mention, as a discussion of this point would carry us far beyond the intent of this paper. Scott found no change in the capacity of platinized platinum with change in pressure, although he used pressures as high as 800 atmospheres. It has recently been shown by several different methods that platinized platinum, saturated with oxygen, does not give the correct potential value for an oxygen electrode.<sup>1</sup> Gordon,<sup>2</sup> as well as Wien,<sup>3</sup> found an apparent increase in the resistance of an electrolytic cell subjected to alternating current polarization, even when this polarization was balanced by capacity or inductance.

CENTRAL UNIVERSITY,  
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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE  
UNIVERSITY OF CHICAGO.]

## THE ABSORPTION COEFFICIENTS OF URANIUM COMPOUNDS.

BY HENRY M. GOETTSCH.

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It was first stated by Mme. Curie<sup>4</sup> that the radioactivity of

<sup>1</sup> Lewis: *This Journal*, 28, 158 (1906).

<sup>2</sup> Gordon: *Loc. cit.*

<sup>3</sup> Wien: *Wied. Ann.* 58, 37 (1896).

<sup>4</sup> Thèse, Paris, 1903: *Chem. News*, 88, 98 (1903).

uranium compounds was an atomic and not a molecular property; the activities found, however, were only very roughly proportional to the percentages of uranium. In her experiments, Mme. Curie took no account of the absorption of the  $\alpha$ -ray activity by the active compound itself. It was shown by McCoy,<sup>1</sup> that it was possible to determine the amount of this absorption, and that by taking it into account, the activity was indeed strictly proportional to the percentage of uranium, and therefore an atomic property. Only three compounds of uranium were investigated by McCoy. It therefore seemed desirable to examine thoroughly in a similar manner a larger number of pure uranium compounds. My results on five other uranium compounds confirm those previously announced by McCoy. The absorption coefficients of a large additional number of uranium compounds were then obtained, indirectly, in an endeavor to find relationships between the absorption and other physical or chemical properties.

The theory of the absorption of the activity within the radioactive film has been given by McCoy.<sup>2</sup> He has shown that

$$k_2 = 2.303 \, s/w \log 1/(1-x),$$

where  $k_2$  is the absorption coefficient for unit weight on unit area;  $x$  is the ratio of the observed activity of a thin film to that of a film of the same substance, of equal area, and sufficiently thick to be of maximum activity;  $w$  is the weight of the thin film; and  $s$  is the area of the films, which in all of these experiments was equal to 39.82 sq. cm. The coefficient,  $k_2$ , differs for different uranium compounds, but is constant for any one compound. These values of  $k_2$  may be used to calculate the total activities of unit weight,  $k_1$ , of each of the compounds examined. If the activity of a film of uranium oxide of maximum activity be taken as unity, and if  $A_1$  represents the maximum activity of a film of any other body as compared with the standard, the following relation holds:

$$k_1 = 2k_2A_1/s.$$

The value of  $k_1$  may be obtained in another way.<sup>3</sup> For an infinitely thin film there would be no absorption, hence

$$A = \frac{1}{2}k_1w, \text{ and } k_1 = 2A/w \quad (1)$$

$$\text{but } x = A/A_1. \text{ Substituting in} \quad (1),$$

$$k_1 = 2A_1x/w.$$

<sup>1</sup> This Journal, 27, 391 (1905).

<sup>2</sup> Loc. cit.

<sup>3</sup> McCoy: Loc. cit.

If the values of  $w$  be plotted along the axis of abscissae, and the ratios of  $w/x$  as ordinates, the point of intersection of the curve with the axis of ordinates gives the value of  $w/x$  for an infinitely thin film. The values of  $k_1$  obtained by the two methods are shown in Tables VII and VIII.

If the radioactivity of uranium compounds is an atomic property,  $k_1/P$  should be a constant, where  $P$  is the weight of uranium in 1 gram of the compound. Complete series of measurements, made on six different uranium compounds, show that the value of  $k_1/P$  is a good constant, and confirm the results previously announced by McCoy.<sup>1</sup>

The mean value for  $k_1/P$  was found to be 19.84. If this value be assumed to hold for all compounds of uranium, it becomes possible to deduce the value of  $k_2$  for any compound by the measurement of the activity of a single film of maximum activity. From the relation  $k_1 = 2k_2A_1/s$ , where  $s = 39.82$ , we obtain  $k_2 = \frac{395P}{A_1}$ . The comparison of the activity of a film of maximum activity with that of the standard oxide gives  $A_1$   $P$  being derived from analysis. The results of these determinations are given in Table IX.

*Methods of Preparation and Analysis.*—For all the preparations used, Kahlbaum's purest uranium nitrate served as the starting material. Since all uranium ores contain radium,<sup>2</sup> it was necessary to show that the nitrate employed was free from radium in quantities sufficient to affect the activity. A large quantity of the nitrate was finely ground in an agate mortar, thoroughly mixed, and a 10-gram sample taken. This was dissolved in 250 cc. of water, warmed to 70°, and then treated with an amount of ammonium carbonate sufficient to redissolve the precipitate first formed. About 2 grams of barium chloride were then added, and a slight excess of ammonium sulphate. After digesting at 70–80° for about an hour, the precipitated barium sulphate was filtered off and dried. This treatment was carried out three times. The activity of the precipitated sulphates was then determined. No. 1 was much the most active, as will be seen from the appended time of discharge of the electroscope.

<sup>1</sup> Loc. cit.

<sup>2</sup> McCoy: Ber. 37, 2641 (1904); Boltwood: Am. J. Sci. 18, 97 (1904); Phil. Mag. [6] 9, 599 (1906).

Sample.	Time of discharge (seconds).
Standard $U_3O_8$ .....	15.75
$BaSO_4$ , No. 1.....	89.
$BaSO_4$ , No. 2.....	431.
$BaSO_4$ , No. 3.....	329.

It was evident from the pale yellow color of the precipitates that they had mechanically carried down uranium. To remove this they were then boiled with 200 cc. of water to which had been added 10 cc. of pure concentrated hydrochloric acid. After digesting the hot solution for an hour, it was filtered, and the residue washed till the wash-water failed to give a test for uranium with potassium ferrocyanide. The precipitates were now pure white, and after drying in the oven were returned to the trays which had been washed and dried. The activity had been diminished greatly.

Sample.	Time of discharge.
Standard $U_3O_8$ .....	15.80
No. 1.....	369.
No. 2.....	3740.
No. 3.....	3991.

The weight of each sulphate precipitate was about 2 grams. The radium is practically removed by the first precipitation. As this amount was obtained from 10 grams of the nitrate, and as the maximum weight of the substances examined rarely exceeded 1.5 grams, it was evident that the amount of radium was too small to affect appreciably the activity of the preparations measured. This conclusion was verified by converting the purified nitrate into the oxide and comparing its activity with that of my standard oxide which had been made by the direct ignition of the commercial nitrate. After making three precipitations as described, I added hydrochloric acid to the filtrate until precipitation began, and then concentrated by boiling down. An orange-yellow, granular precipitate fell out, which was easy to filter and wash. It was probably a mixture of ammonium uranate and ammonium carbonate. After drying, the precipitate was ignited, at first gently, in a porcelain crucible. After most of the moisture and ammonia had been driven off, the residue was transferred to a platinum crucible and the ignition finished in oxygen. About 5.2 grams of pure black oxide,  $U_3O_8$ , were obtained. From it a film was prepared, sufficiently thick to be of maximum activity. By comparison with the standard oxide their activities were found to be practically identical.



Sample.	w	Time of discharge.
Standard.....	0.5637	15.75
"Purified" sample.....	0.5671	15.80

The result showed that the nitrate was sufficiently pure to be used directly in the preparation of the compounds to be tested.

A large number of methods for the determination of uranium were tried. In many compounds containing no other fixed substances, simple ignition converts the uranium into urano-uranic oxide,  $U_3O_8$ . In using this method it is necessary to finish the ignition in oxygen, since the researches of Zimmermann<sup>1</sup> have shown that when the ignition is done in air, there is a slow loss of oxygen. The color of the residue varies with the degree of heat, from a dark green if ignited at bright redness, to a pure black when the highest temperature of the blast lamp is employed. The composition, according to the same author, does not vary. I have found that thick films, prepared from both the green and the black oxides, have the same activity.

In acid solutions, in the presence of alkalies or alkaline earths, uranium may be precipitated as ammonium uranate,  $(NH_4)_2U_2O_7$ , which on ignition gives the oxide. The precipitate is always contaminated with considerable amounts of the other metals; however, as Hillebrand<sup>2</sup> has shown, and Kern<sup>3</sup> has confirmed, the uranate may be obtained free from alkalies or alkaline earths by redissolving and reprecipitating twice. The method is somewhat tedious, but gives good results. The separation of uranium from barium, by precipitation of the former as uranyl ammonium phosphate, as recommended by Kern,<sup>4</sup> was found unsatisfactory. A considerable amount of barium was carried down. A better separation from alkaline earths was afforded by electrolytic methods. Kollock and Smith<sup>5</sup> have shown that uranium is deposited on the cathode as a hydrated oxide from acetic acid solutions, molybdenum being the only other metal showing a similar behavior. Kern also has investigated the method, and the directions given by him were followed with good results.

For analysis, material was taken from some of the thicker films, after completing measurements upon their activity. In this

<sup>1</sup> Ann, 232, 276 (1885).

<sup>2</sup> Am. J. Sci. 10, 136 (1900).

<sup>3</sup> This Journal, 23, 708 (1901).

<sup>4</sup> Ibid.

<sup>5</sup> Ibid. 23, 607 (1901).

way the results of the analysis would more accurately represent the uranium content of the films in the condition of actual use, since small changes of composition, due to gain or loss of moisture, would be accounted for. The films were usually kept in the open air, carefully protected from dust; in some cases, where a tendency to absorb moisture was observed, they were kept in desiccators.

The gravimetric determination of uranium being rather tedious, recourse was often had to the volumetric process. The comments on this process as given in the literature are of a conflicting character. The reduction of uranium solutions with zinc and sulphuric acid and titration with permanganate is due to Belouhoubeck.<sup>1</sup> Guyard<sup>2</sup> states that the results are always inexact, and he ascribes this to the formation of lower suboxides of uranium. Zimmermann,<sup>3</sup> who next took up the process, states that these suboxides do not exist, that uranyl salts are not reduced beyond  $\text{UO}_2$ , and that they admit of most exact determination by permanganate. He carried out his reductions in a flask provided with a Bunsen valve, and found that half an hour was sufficient for the reduction of rather large quantities. He also found that the oxidation of uranous salts exposed to the air occurred but slowly, so that the error from that cause became inappreciable in rapid work. Kern<sup>4</sup> has published the results of numerous experiments with the process. He finds, in agreement with Zimmermann, that the reduction does not proceed beyond the tetravalent stage, even when prolonged for five hours. To prevent a possible reoxidation in the air, he works in an atmosphere of carbon dioxide, by pouring the reduced acid liquid into the titrating flask which contained some sodium carbonate. In opposition to these statements, Pulman<sup>5</sup> finds that the reduction does proceed partly beyond the tetravalent stage. He finds, however, that this may be corrected by dispensing with the atmosphere of carbon dioxide, and allowing the solution to drip from the reductor into the titrating dish, all the time freely exposed to the air. In this way the part reduced beyond the  $\text{UO}_2$  stage, is oxidized back without any tendency to oxidize further. The time of reduction was one hour.

<sup>1</sup> Z. anal. Chem. 6, 120 (1867).

<sup>2</sup> Bull. soc. chim. 1, 94.

<sup>3</sup> Ann. 213, 300 (1882).

<sup>4</sup> This Journal, 23, 712 (1901).

<sup>5</sup> Am. J. Sci. [4] 16, 229 (1903).

In agreement with the work of Pulman, I found that the results were not uniform when Kern's directions were followed, but that they often came high, showing that the reduction did proceed too far. This was also indicated by the color of the solution which finally became a dirty brownish green. The method of work finally adopted was one recommended by Prof. McCoy, who had used it in work on uranium ores. In view of the uniformly good results given by the method, and its rapidity of execution, it seems worth while to give the details of the process.

The reductions were carried out in a large beaker of about one liter capacity. One hundred grams of pure stick zinc were introduced in the form of 15 to 20 small pieces; then the uranium compound was added, dissolved in dilute sulphuric acid and in amount equivalent to 0.100–0.150 gram of metallic uranium; finally the volume of the liquid was brought to about 125 cc., of a concentration corresponding to one part of acid, sp. gr. 1.84, to five parts of water, by volume. The beaker was then covered with a watch-glass and the solution heated to boiling. After boiling began, the heat was so regulated as to maintain about 1 cm. of thick foam over the boiling solution.

Under these conditions the reduction proceeds with great rapidity. It was often complete in two minutes, and never took more than five, and could be continued for a quarter of an hour without affecting the result. The color of the solution changes from yellow through various shades of green to a muddy brownish green, which indicates the completion of the reaction. The sides of the beaker were rinsed with water and the hot solution decanted through a filter into a large evaporating dish. The zinc was rapidly rinsed with cold water, and the washings also run through. The color changes almost instantly to a pale olive-green. About five minutes were taken up with the filtration. The final volume of the solution just before titration was about 500 cc. The titration was then carried out, using approximately  $N/30$  permanganate, which had been standardized against metallic iron, and also against pure  $U_3O_8$ , the two methods giving practically identical results. The results of the titration were not appreciably different if the solution was allowed to stand fifteen minutes before running in the permanganate. This method was used in the analysis of many of the compounds, and

as only bodies of apparently well established composition were used, besides uranium no other constituents were as a rule determined. Twenty-six uranium compounds were prepared and analyzed; the details are given elsewhere.<sup>1</sup> In that which follows, the formulas given for the various compounds are those indicated by the analyses.

In cases where a different method of analysis was followed, this is mentioned in connection with the preparation of the compound.

*Determination of Radioactivity.*—The method of work used was the one developed by McCoy.<sup>2</sup> The substance under examination was very finely ground with a volatile liquid in an agate mortar. Chloroform and alcohol proved the most generally useful, but ether, ligroin, benzene and carbon bisulphide were also used. After grinding, the mixture was transferred to a small beaker and then, while still in suspension, rapidly poured into a circular shallow, tinned iron tray. These trays, which were 7.12 cm. in diameter, with rims 0.8 cm. high,<sup>3</sup> were intended for covers for jelly glasses, and were easily obtained in quantity. A cover glass was placed over the tray, until the solid matter had settled; the liquid was then allowed to evaporate spontaneously. When alcohol was used, it sometimes happened that on account of the slow evaporation, the metal trays became rusty before the films were dry. This was avoided by placing under a large inverted crystallizing dish, along with the evaporating sample, trays of fused calcium chloride. This very rapidly absorbed both alcohol and water, and proved of great assistance in getting smooth and uniform films. The measurements of the activity were made with an electroscope of the C. T. R. Wilson type,<sup>4</sup> but having in addition a horizontal metal plate 5 cm. in diameter attached to the vertical strip carrying the aluminium leaf. The measurement consisted in noting with a stop-watch the time of discharge of the leaf of the electroscope across ten divisions of the scale of

<sup>1</sup> Dissertation, Univ. of Chicago, 1906.

<sup>2</sup> Loc. cit.

<sup>3</sup> It might be thought that an error in the determination of the activity would result from the absorption of a portion of the rays by the rims, but as all of the trays had rims of the same height, the same fraction of the activity would be absorbed in the case of every film, including the standard. No error was incurred on this account.

<sup>4</sup> *Phil. Mag.* 66, 152 (1901).

the micrometer microscope. The potentials corresponding to the beginning and end of the ten divisions were 200 and 150 volts, respectively. The natural leak of the electroscope remained quite constant. Observations at different times during a period of several months showed the time of discharge of the empty electroscope to be from eight to ten hours. After being in continual use for over a year, the time of leak had diminished to about five hours. It was therefore necessary to make corrections for the natural leak. With an active sample, the minimum time of discharge was found for a distance, between the active sample and the charged plate of the electroscope, of 34 mm. This distance was used in all of the following measurements.

Four determinations of the activity of each film were made and the average taken. These determinations were repeated on different days, and the mean of three or more different measurements taken for the final value. To compensate for any change of sensitiveness of the electroscope, measurements were made on the standard sample immediately before and after the measurements made with each film. The mean of these was used to compare with the activity of the film to deduce the value of  $x$ . In this manner, complete measurements were made for a series of films of six different compounds. The results are given in Tables I-VI.

TABLE I.—URANO-URANIC OXIDE,  $U_3O_8$ 

No	$w$ .	$r$ .	$w/r$ .	$k_2$ .
1 (Standard) .....	0.5637	1.000	0.5637	....
2.....	0.2936	0.945	0.3108	....
3.....	0.2148	0.853	0.2519	355
4.....	0.2101	0.822	0.2556	327
5.....	0.1678	0.749	0.2241	328
6.....	0.0966	0.549	0.1760	328
7. ....	0.0873	0.518	0.1686	333
8.....	0.0736	0.460	0.1600	334
9.....	0.0486	0.324	0.1500	321
10. ....	0.0418	0.293	0.1427	331
11.....	0.0244	0.176	0.1387	316
12.....	0.0147	0.117	0.1256	338
13.....	0.0110	0.088	0.1250	334
14.....	0.0078	0.061	0.1278	321

Mean, 331

The value found by McCoy was 335. The results are in good agreement and show themselves in no way dependent upon the

sample or the instruments used, thus furnishing a further proof of the correctness of the theory.

TABLE II.—URANIC ACID,  $H_2U_2O_7$ .

No.	<i>w.</i>	<i>x.</i>	<i>w/x.</i>	<i>k<sub>2</sub>.</i>
1.....	0.5160	Maximum	0.516	.....
2.....	0.2927	0.983	0.2977	.....
3.....	0.2345	0.884	0.2653	366
4.....	0.1671	0.772	0.2165	353
5.....	0.1468	0.740	0.1985	365
6.....	0.1412	0.730	0.1934	369
7.....	0.1274	0.691	0.1844	367
8.....	0.0624	0.432	0.1444	361
9.....	0.0503	0.372	0.1352	367
				Mean, 364

Benzene was used as the suspending liquid. It was not possible to obtain uniform films thinner than No. 9. Attempts were made with chloroform, ligroin and alcohol, as suspending liquids, but the films presented peculiar mottled and striped effects. This is probably a result of surface tension and was a difficulty repeatedly encountered.

TABLE III.—URANYL IODATE,  $UO_2(IO_3)_2 \cdot H_2O$ .

No.	<i>w.</i>	<i>x.</i>	<i>w/x.</i>	<i>k<sub>2</sub>.</i>
1.....	0.9282	Maximum		
2.....	0.6916	"	0.6916	.....
3.....	0.4790	0.986	0.4857	....
4.....	0.4039	0.971	0.4160	.....
5.....	0.2617	0.937	0.2793	421
6.....	0.2160	0.889	0.2430	400
7.....	0.2048	0.885	0.2314	421
8.....	0.1555	0.790	0.1968	400
9.....	0.1463	0.782	0.1879	413
10.....	0.1048	0.673	0.1557	425
11.....	0.0660	0.502	0.1314	421
12.....	0.0450	0.364	0.1236	401
				Mean, 413

Alcohol was used as the suspending liquid in making films of the iodate.

TABLE IV.—URANYL THIOSULPHATE,  $\text{UO}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ .

No.	<i>w.</i>	<i>x.</i>	<i>w/x.</i>	<i>k<sub>2</sub>.</i>
1.....	0.5539	Maximum		
2.....	0.4404	"	0.4404	
3.....	0.3771	0.977	0.3859	.....
4.....	0.2334	0.932	0.2504	.....
5.....	0.2278	0.914	0.2492	428
6.....	0.2134	0.887	0.2406	407
7.....	0.1517	0.817	0.1857	446
8.....	0.1475	0.805	0.1832	441
9.....	0.1211	0.740	0.1636	443
10.....	0.1043	0.674	0.1547	428
11.....	0.0903	0.621	0.1454	428
12.....	0.0715	0.537	0.1331	429
				Mean, 431

The thiosulphate films were made by the use of chloroform as suspending liquid.

TABLE V.—SODIUM URANATE,  $\text{Na}_2\text{U}_2\text{O}_7$ .

No.	<i>w.</i>	<i>x.</i>	<i>w/x.</i>	<i>k<sub>2</sub>.</i>
1.....	0.9443	Maximum		
2.....	0.5315	0.985	0.5396	.....
3.....	0.2539	0.901	0.2818	363
4.....	0.1750	0.793	0.2207	358
5.....	0.1738	0.787	0.2208	355
6.....	0.1518	0.744	0.2040	358
7.....	0.1487	0.740	0.2010	361
8.....	0.1089	0.622	0.1751	356
9.....	0.0866	0.562	0.1541	380
10.....	0.0841	0.502	0.1675	338
11.....	0.0634	0.433	0.1464	356
12.....	0.0458	0.338	0.1355	358
13.....	0.0457	0.337	0.1356	358
14.....	0.0382	0.285	0.1341	350
				Mean, 358

A mixture of chloroform and alcohol was used as the suspending liquid for the films of sodium uranate.

TABLE VI.—URANYL AMMONIUM PHOSPHATE,  $\text{UO}_2\text{NH}_4\text{PO}_4 \cdot 3\text{H}_2\text{O}$ .

No.	w.	x.	w/x.	k <sub>2</sub> .
1.....	0.9813	Maximum		
2.....	0.9749	"		
3.....	0.4788	0.974	0.4915	.....
4.....	0.2088	0.923	0.2262	489
5.....	0.1984	0.917	0.2164	504
6.....	0.1939	0.910	0.2131	495
7.....	0.1660	0.887	0.1872	524
8.....	0.1494	0.847	0.1764	501
9.....	0.1229	0.790	0.1555	506
10.....	0.1078	0.749	0.1440	511
11.....	0.1040	0.735	0.1415	508
12.....	0.0791	0.632	0.1251	492
13.....	0.0773	0.624	0.1239	515
14.....	0.0483	0.451	0.1071	495
15.....	0.0347	0.347	0.1000	489

Mean, 502

A mixture of alcohol and chloroform was used as the suspending liquid.

The values of  $k_2$  given in the preceding tables may now be used to calculate the values of  $k_1$  and  $k_1/P$  for the different compounds examined. The values as obtained by the first method are given in Table VII.

TABLE VII.

Substance.	A'.	k <sub>2</sub>	k <sub>1</sub>	100P.	k/P.
Urano-uronic oxide .....	1.000	331	16.63	84.82	19.60
Uranic acid .....	0.876	364	16.01	80.73	19.82
Uranyl iodate .....	0.356	413	7.37	37.15	19.86
Uranyl thiosulphate.....	0.533	431	11.53	57.32	20.10
Sodium uranate.....	0.816	358	14.67	74.27	19.74
Uranyl ammon. phosphate..	0.431	502	10.86	54.68	19.93

Mean, 19.94

We may compare with these values those obtained by McCoy.<sup>1</sup>

Urano-uronic oxide .....	1.000	335	16.69	84.90	19.7
Uranyl oxalate .....	0.459	507	11.59	57.60	20.1
Ammonium uranate.....	0.720	417	14.95	74.40	20.1

Mean, 20.0

The values of McCoy are for  $S=40.15$ . In order to compare them with my results we must multiply them by the ratio between

<sup>1</sup> This Journal, 27, 391 (1905).



the areas of the trays used. The value then found for  $k_1/P$  is  $\frac{40.15}{39.82} \times 20.0 = 20.16$ .

The value of  $k_1/P$ , which represents the total activity of unit weight of metallic uranium, should be constant, if radioactivity is an atomic property. The result is in harmony with the theory.

In Table VIII are given the values of  $k_1$  as obtained by graphic extrapolation. The values of  $w/x$  are taken from curves, which were similar to those obtained by McCoy.<sup>1</sup> In the fourth column are given for comparison the values of  $k_1$  as found by the first method. The greatest deviation is about 1 per cent.

TABLE VIII.

Substance.	$(w/x)_0$ .	$A^1$	$k_1$ .	$\langle k_1 \rangle$ .	$k_1/P$ .
Urano-uranic oxide.....	0.120	1.000	16.66	16.63	19.64
Uranic acid.....	0.110	0.876	15.92	16.01	19.72
Uranyl iodate.....	0.095	0.356	7.49	7.37	20.17
Uranyl thiosulphate.....	0.093	0.533	11.47	11.53	19.99
Sodium uranate.....	0.112	0.816	14.57	14.67	19.62
Uranyl ammon. phosphate.	0.080	0.431	10.77	10.86	19.71

Mean, 19.81

The mean value of  $k_1/P$  is practically identical with that found before (19.84). The value 19.84 will be taken as the most probable value of the constant. If the unit of activity is taken as that due to 1 sq. cm. of a thick film of  $U_3O_8$ , instead of that due to the whole standard film, the value of  $k_1/P$  becomes  $19.84 \times s$ . Since  $s$ , the area of the films, was 39.82 sq. cm.,  $k_1/P = 790$ . Therefore, the total activity of 1 gram of uranium is 790 times that of 1 sq. cm. of a thick film of  $U_3O_8$ .

In Table IX are given the absorption coefficients of all the compounds examined. In the case of six of the compounds they were obtained by direct measurements of a series of films; in all other cases they were derived by calculation, by means of the equation  $k_2 = 395P/A_1$  from the measured value of the activity,  $A_1$ , of a film of maximum activity. In most cases a film of 0.5 gram in weight was sufficient to give the maximum activity, but in every case several films were prepared, ranging in weight from about 0.7 to 1.5 grams. When several thick films of different weight but of equal activity were obtained, the resulting activity was taken as the maximum.

<sup>1</sup> This Journal, 27, 391 (1905).

TABLE IX.

Substance.	100 P.	A'.	$k_1$ .	$k_2$ .
Uranium (Merck) (impure) . . . . .	90.00	1.18	17.85	301
Uranium (E. & A.) (impure) . . . . .	90.20	1.20	17.89	297
Uranium dioxide . . . . .	88.16	1.126	17.50	310
Urano-uranic oxide . . . . .	84.82	1.000	16.63	331
Uranic acid . . . . .	80.73	0.876	16.01	364
Sodium uranate . . . . .	74.27	0.816	14.67	358
Potassium uranate . . . . .	70.03	0.765	13.90	362
Calcium uranate . . . . .	74.00	0.785	14.70	373
Strontium uranate . . . . .	66.88	0.651	13.27	406
Barium uranate . . . . .	58.63	0.591	11.63	392
Uranyl sodium acetate . . . . .	50.81	0.357	10.05	562
Uranyl potassium acetate . . . . .	49.04	0.339	9.74	573
Uranyl lead acetate . . . . .	31.24	0.250	6.20	494
Uranyl barium acetate . . . . .	44.64	0.320	8.87	551
Uranyl nitrate ( $2\frac{1}{2}H_2O$ ) . . . . .	54.43	0.436	10.80	493
Uranyl nitrate ( $3\frac{1}{2}H_2O$ ) . . . . .	52.24	0.411	10.36	502
Uranyl potassium nitrate . . . . .	48.25	0.369	9.57	517
Uranyl sulphate . . . . .	55.73	0.446	11.02	492
Uranous sulphate . . . . .	46.10	0.362	9.15	504
Uranyl potassium sulphate . . . . .	40.60	0.302	8.06	531
Uranyl oxalate . . . . .	57.60	0.459	11.59	507
Uranyl potassium oxalate . . . . .	41.20	0.280	8.18	582
Uranyl potassium propionate . . . . .	45.00	0.297	8.93	599
Uranyl potassium butyrate . . . . .	41.65	0.260	8.26	633
Uranyl thiosulphate . . . . .	57.32	0.533	11.53	431
Uranyl ammonium phosphate . . . . .	54.68	0.431	10.86	502
Uranyl iodate . . . . .	37.15	0.356	7.37	413
Uranyl potassium chloride . . . . .	45.10	0.352	8.95	506
Uranyl potassium carbonate . . . . .	38.64	0.285	7.60	531

The values found above for the absorption coefficient of metallic uranium cannot be taken as more than a rough approximation to the true value.

*Summary.*—The theory of the absorption of radioactivity of uranium compounds, as developed by McCoy,<sup>1</sup> is shown to hold accurately in the case of the six compounds examined. It is proven that absorption is not dependent on the form of the measuring instrument, and that measurements can be accurately duplicated. The theory that radioactivity is an atomic phenomenon receives additional confirmation in the good constant found for the value of  $k_1/P$ . The absorption is not proportional to the molecular weight. This is readily seen in the case of the

<sup>1</sup> Loc. cit.

black oxide which has a low absorption with a very high molecular weight. It is very probable that absorption, like radioactivity, is an atomic phenomenon. A fuller discussion of this question is given in a later paper by Prof. McCoy and myself.

This work was undertaken at the suggestion of Dr. H. N. McCoy, and carried out under his guidance. It is a pleasant duty, in concluding, to express to him my gratitude for his unfailing interest in the work, and for the many helpful suggestions received.

May, 1906

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE ABSORPTION OF THE $\alpha$ -RAYS OF URANIUM.

BY HERBERT N. MCCOY AND HENRY M. GOETTSCH.

Received August 4, 1906.

If  $k_2$  is the absorption coefficient (referred to unit weight upon unit area) of the  $\alpha$ -rays of any uranium compound, it is found<sup>1</sup> that

$$A = A_1 (1 - e^{-\frac{k_2 w}{s}}). \quad (1)$$

where  $A$  is the activity of a *uniform, thin* film of the compound, of weight  $w$  and area  $s$ , and  $A_1$  is the activity of a film of the same compound of equal area and sufficiently thick to be of maximum activity. If  $\frac{A}{A_1} = x$ , then

$$k_2 = \frac{2.303 s}{w} \log \frac{1}{1-x}. \quad (2)$$

Calling  $k_1$  the *total* activity of unit mass of the active compound,

$$k_1 = \frac{2k_2 A_1}{s}. \quad (3)$$

In the paper referred to, results were given for three uranium compounds. The values found for  $k_2$  were constant for each compound, but different for different compounds. The values of  $k_1$  as found from those of  $k_2$  by the above equation, were strictly proportional to the uranium content,  $P$ , of the compound. This investigation has now been extended by one of us.<sup>2</sup> Table I gives a summary of both series of measurements.

<sup>1</sup> McCoy: This Journal, 27, 391 (1905).

<sup>2</sup> Goettsch: Preceding paper.

TABLE I.

Series I (McCoy). $s = 40.15$ sq. cm.					
Substance.	$A_1$ .	$k_2$ .	$k_1$ .	P.	$k_1/P$ .
$U_3O_8$ .....	1.000	335	16.69	0.8482	19.7
$(NH_4)_2U_2O_7$ .....	0.720	417	14.95	0.744	20.1
$UO_2C_2O_4 \cdot 3H_2O$ .....	0.459	507	11.59	0.576	20.1
					Mean, 20.0
Series II (Goettsch). $s = 39.82$ sq. cm.					
Substance.	$A_1$ .	$k_2$ .	$k_1$ .	P.	$k_1/P$ .
$U_3O_8$ .....	1.000	331	16.63	0.8482	19.60
$UO_2$ .....	0.876	364	16.01	0.8073	19.82
$Na_2U_2O_7$ .....	0.816	358	14.67	0.7427	19.74
$UO_2(IO_3)_2 \cdot H_2O$ .....	0.356	413	7.37	0.3715	19.86
$UO_2NH_4PO_4 \cdot 3H_2O$ .....	0.431	502	10.86	0.5468	19.93
$UO_2S_2O_8 \cdot 2H_2O$ .....	0.533	431	11.53	0.5732	20.10
					Mean, 19.84

In Table I the values of  $A_1$  and  $k_1$  are expressed, in each series, in terms of the activity of a thick film of  $U_3O_8$  as unity. If, instead, the activity of 1 sq. cm. of such a standard film of  $U_3O_8$  be taken as the unit,<sup>1</sup> then  $\frac{k_1 s}{P}$  will represent the total activity of 1 gram of uranium, in terms of this unit. For the first series  $\frac{k_1 s}{P}$  equals 803; for the second, 789. Considering also the other values found by each of us separately by another method,<sup>2</sup> we have taken 790 as the most probable value of this constant. The total activity of 1 gram of uranium is independent of its form of chemical combination and equal to 790 times the activity due to 1 sq. cm. of a film of pure  $U_3O_8$  sufficiently thick to be of maximum activity.

Assuming that this relation holds true for every pure uranium compound, as in all probability it does, we may determine the absorption coefficient,  $k_2$ , of any uranium compound from a knowledge of the activity,  $A_1$ , of a single thick film, of maximum activity.

$$k_2 = \frac{395 P}{A_1} \quad (4)$$

The values of  $k_2$  so found, together with those determined directly, are given in Table II, first column. The highest ab-

<sup>1</sup> McCoy: Phil. Mag. [6] 11, 176 (1906).

<sup>2</sup> McCoy: Loc. cit.

sorption coefficient, that of potassium uranyl butyrate, is more than twice as great as the lowest, that of uranous oxide. The magnitude of the absorption coefficient depends upon the chemical composition of the compound. Absorption is found to be an atomic property; for each element, independent of its form of chemical combination, there is a definite absorption coefficient.

TABLE II.

	$k_2$ obs.	$k_2$ calc.	$\Sigma \frac{P}{\sqrt{w}}$	C.	$A_1$ obs.	$A_1$ calc.
$\text{UO}_2$ .....	310	288	0.0866	3580	1.126	1.210
$\text{U}_3\text{O}_8$ .....	331	310	0.0930	3560	1.000	1.081
$\text{Na}_2\text{U}_2\text{O}_7$ .....	358	364	0.1093	3280	0.816	0.808
$\text{K}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}$ .....	362	371	0.1116	3240	0.765	0.745
$\text{UO}_3$ .....	364	335	0.1006	3620	0.876	0.952
$\text{CaU}_2\text{O}_7 \cdot \text{H}_2\text{O}$ .....	373	367	0.1103	3380	0.785	0.796
$\text{BaU}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ .....	392	396	0.1186	3310	0.591	0.585
$\text{SrU}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ .....	406	382	0.1149	3530	0.651	0.692
$\text{UO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ .. .	413	396	0.1191	3470	0.356	0.370
$\text{NH}_4\text{U}_2\text{O}_7$ .. .	417	414	0.1178	3350	0.714	0.705
$\text{UO}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ .....	431	469	0.1408	3060	0.533	0.483
$\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ .....	492	512	0.1535	3200	0.362	0.327
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ....	493	530	0.1589	3100	0.436	0.406
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ ....	502	552	0.1654	3030	0.411	0.374
$\text{UO}_2\text{NH}_4\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ....	502	567	0.1619	3100	0.431	0.381
$\text{K}_2\text{UO}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ .....	506	454	0.1364	3710	0.352	0.392
$\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ .....	507	519	0.1560	3250	0.455	0.438
$\text{KUO}_2(\text{NO}_3)_3$ .....	517	517	0.1552	3330	0.369	0.368
$\text{K}_4\text{UO}_2(\text{CO}_3)_3$ .....	531	524	0.1572	3380	0.285	0.291
$\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ....	531	527	0.1582	3360	0.302	0.304
$\text{BaUO}_3(\text{C}_6\text{H}_5\text{O}_2)_6 \cdot 2\text{H}_2\text{O}$	551	557	0.1669	3300	0.320	0.317
$\text{NaUO}_3(\text{C}_6\text{H}_5\text{O}_2)_3$ .....	561	578	0.1742	3220	0.357	0.347
$\text{KUO}_3(\text{C}_6\text{H}_5\text{O}_2)_3$ .....	573	570	0.1718	3340	0.339	0.340
$\text{K}_2\text{UO}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ ...	582	573	0.1723	3380	0.280	0.284
$\text{KUO}_2(\text{C}_6\text{H}_5\text{O}_2)_3$ .....	599	629	0.1891	3110	0.297	0.283
$\text{KUO}_2(\text{C}_6\text{H}_7\text{O}_2)_3$ .....	633	679	0.2038	3170	0.260	0.242

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Mean, 3330

If  $P$  is the weight of any element in 1 gram of a uranium compound, and  $k$  is the absorption coefficient of that element,  $kP$  is the partial absorption due to that element and the sum of all such partial values, or  $\Sigma kP$ , is equal to the absorption coefficient of the compound. That is

$$\Sigma kP = k_2. \quad (5)$$

The coefficients for uranium and oxygen,  $k_u$  and  $k_o$ , may be

calculated by means of equation (5) from the absorption coefficients of the oxides  $\text{UO}_2$  and  $\text{UO}_3$ , which have 88.2 and 80.7 per cent. of uranium respectively.

$$0.882 k_u + 0.118 k_o = 310$$

$$0.807 k_u + 0.193 k_o = 364.$$

Therefore  $k_u = 225$  and  $k_o = 864$ . From these values the coefficient of  $\text{U}_3\text{O}_8$  (84.8 per cent. of uranium) is calculated to be 322, which is in good agreement with the value found, 331.

It is found that the product of the absorption coefficient of any element by the square root of its atomic weight is very nearly constant. Thus for uranium,  $225 \times \sqrt{238.5} = 3476$ ; and for oxygen,  $864 \times \sqrt{16} = 3456$ . Calling this constant C, and the atomic weight of any element W,

$$k\sqrt{W} = C. \quad (6)$$

Equations (5) and (6) give

$$k_2 = C \left( \sum \frac{P}{\sqrt{W}} \right), \quad (7)$$

and

$$C = \frac{k_2}{\sum \frac{P}{\sqrt{W}}}. \quad (8)$$

The fourth column of Table II contains the values of C calculated by equation (8). The mean value of the constant, C, for all determinations is 3330. The average deviation from the mean is 4.9 per cent. Column 2 of Table II contains the values of  $k_2$  as calculated by means of equation (7) which now becomes

$$k_2 = 3330 \sum \frac{P}{\sqrt{W}}. \quad (7a)$$

The activity,  $A_1$ , of a thick film of any uranium compound may be calculated in a very simple way from its composition. Equations (4) and (7a) give by combination,

$$A_1 = \frac{0.1186 P_u}{\sum \frac{P}{\sqrt{W}}}. \quad (9)$$

The last two columns of Table II give the values of  $A_1$  as directly observed and as calculated by equation (9). The average difference between the values of  $k_2$  or of  $A_1$  as observed and as calculated is 4.9 per cent. There are at least three possible sources of experimental error: (1) the measurement of radioactivity; (2) the presence of UX; (3) the determination of the composition. It is probable that the experimental error involved in the determination of the activity of any film in terms of the standard is not over

one per cent. in any case. All of our experiments have been made with uranium from which UX had not been removed. The ionization due to the  $\beta$ -rays of UX is very slight, but has not been deducted. Some of the divergencies from the square-root law of absorption may therefore be due to the effect of the  $\beta$ -rays. Most of the substances studied were analyzed for uranium only and the percentages of the other constituents calculated from the chemical formulas. This procedure involved, of course, appreciable errors in cases of compounds not strictly pure and free from absorbed moisture. The results, here presented, are to be considered as preliminary; we are therefore not able at present to decide whether the square root law is exact or only approximate.

The absorption of the  $\alpha$ -rays in the active film itself is closely connected with the "loss of range"<sup>1</sup> of  $\alpha$ -rays in their passage through a screen of inert matter, covering the radioactive film. Bragg and Kleeman<sup>2</sup> have found, for  $\alpha$ -rays, that the "loss of range" in passing through an atom of such a screen is an additive atomic property, which is independent of the state of chemical combination and proportional to the square-root of the atomic weight. There would, therefore, seem to be a very intimate relationship between "loss of range" and absorption, yet Bragg and Kleeman are of the opinion that the ordinary conception of an absorption coefficient for  $\alpha$ -rays is erroneous. But our own results on the determination of absorption coefficients of pure uranium compounds have shown such good agreement with the logarithmic law of absorption that we can not avoid thinking that the law is, at least, very approximately correct.

Recently Marckwald<sup>3</sup> has made the interesting observation that certain very fluorescent double salts of uranium, notably the double nitrate with potassium, send out light rays. He determined this by the photographic method. When the salt was tested in the electroscope by Marckwald, the activity was found to be of the order of magnitude to be expected, judging from the activity of the simple nitrate. Marckwald inclines to the view that the emission of light is to be explained by the con-

<sup>1</sup> The range is the maximum distance from the active film at which the rays produce gaseous ionization.

<sup>2</sup> Phil. Mag. [6] 10, 318 (1905).

<sup>3</sup> Ber. 39, 200 (1906).

version of a part of the radioactivity into luminous energy. We have found the direct determination of  $k_1$  and  $k_2$  for potassium uranyl nitrate to be impracticable, on account of the impossibility of making uniform thin films. The activity of a thick film was found to be 0.369, which is in almost exact agreement with the calculated value, 0.368 (Table II). It is therefore probable that the proportion of radioactive energy converted into luminous energy is, at most, very small.

Our conclusions may be summarized as follows:

(1) Absorption of radioactivity is, like activity itself, an atomic property, independent of the form of chemical combination.

(2) The absorption by unit weight per unit area is, for any element, inversely proportional to the square-root of its atomic weight.

(3) The radioactivity of a thick film of any pure uranium compound may be calculated from a knowledge of its chemical composition.

## A REVISION OF THE ATOMIC WEIGHT OF MANGANESE.

BY GREGORY PAUL BAXTER AND MURRAY ARNOLD HINES

Received August 2, 1906.

THE following table, taken from Clarke's "A Recalculation of the Atomic Weights"<sup>1</sup> gives a brief resumé of previous work upon the atomic weight of manganese which has other than historical interest.

$$\text{O} = 16.000$$

Berzelius: Ann. Physik. Chem. 18, 74 (1830).	
MnCl <sub>2</sub> : 2AgCl .....	55.12
Turner: Trans. Roy. Soc. Edinb. 11, 143 (1831).	
MnCl <sub>2</sub> : 2AgCl .....	54.92
Dumas: Ann. Chem. Pharm. 113, 25 (1860).	
MnCl <sub>2</sub> : 2Ag.....	54.98
von Hauer: J. pr. Chem. 72, 360 (1857).	
MnSO <sub>4</sub> : MnS.....	54.91
Schneider: Ann. Physik. Chem. 107, 605 (1859).	
Mn : 2CO <sub>2</sub> .....	54.03
Rawack: Ibid.	
Mn <sub>3</sub> O <sub>4</sub> : H <sub>2</sub> O.....	54.08
Dewar and Scott: Proc. Roy. Soc. 35, 44 (1883).	
AgMnO <sub>4</sub> : AgMnO.....	54.86

<sup>1</sup> Smith. Misc. Coll., Constants of Nature, Part, V, p. 283 (1897).



AgMnO <sub>4</sub> : 2KBr.....	55.02
Marignac: Arch. sci. phys. nat. [3] 10, 21 (1883).	
MnO : MnSO <sub>4</sub> .....	55.01
Weeren: Dissertation, Halle (1890).	
MnO : MnSO <sub>4</sub> .....	55.00
MnS : MnSO <sub>4</sub> .....	55.00

From these results Clarke computes the most probable value to be 54.987.

The close agreement of the greater part of these determinations is striking, the experiments of Schneider and Rawack being the only ones which indicate a value for manganese very different from 55.0. The variations of their results from the others is not surprising, however, since manganoso-manganic oxide and manganous oxalate, with which they worked, are undoubtedly difficult to obtain in a pure condition. The remaining determinations all fall within limits 0.26 of a unit apart, and all but two agree within 0.16 of a unit. Our present knowledge concerning the variety of atomic weights upon which the above determinations are based is not sufficiently certain<sup>1</sup> to lead to the expectation of closer agreement from such widely different methods.

For this investigation the substances chosen for examination were manganous chloride and bromide, since the analysis of halogen compounds may be effected with great accuracy. Furthermore, these compounds have not been investigated by any of the more recent experimenters except Dewar and Scott,<sup>2</sup> who performed one analysis each of the chloride and bromide and obtained the values 54.91 and 54.97 respectively.

#### PURIFICATION OF MATERIALS.

*Water.*—All of the water used in either the purification or the analyses was twice distilled, once from a dilute alkaline solution of potassium permanganate and then from a very dilute sulphuric acid solution. Block-tin condensers were used in both distillations and the apparatus contained no rubber or cork connections. The water was collected as a rule in Jena glass flasks, although for special purposes either platinum or quartz receivers were substituted.

*Reagents.*—Acids and ammonia also were distilled shortly

<sup>1</sup> Richards and Wells: Publications of the Carnegie Institution, No. 28, 67 (1905); Report of the International Committee on Atomic Weights, this Journal, 28, 6 (1906).

<sup>2</sup> Loc. cit.

before use, either platinum or quartz condensers and receivers being employed when necessary. Solid reagents were recrystallized, usually with centrifugal drainage.

*Vessels.*—Special pains were taken in all the work to prevent the introduction of alkalis or silica into the purest materials, by avoiding as far as possible the use of glass vessels.

*Manganous Bromide.*—Four different specimens of manganous bromide were employed, which were obtained from different sources and were purified in different ways. In the case of Samples A and B, purification of the manganese from other heavy metals was accomplished by recrystallization of Merck's "chemically pure" potassium permanganate. Sample A was crystallized three times only, while Sample B was thus treated ten times, the last two crops of crystals being thoroughly drained from the mother-liquors by means of a centrifugal.

In order to free the manganese from potassium and convert it into the bromide, the following processes were employed with Sample A: First the permanganate was dissolved in water and was reduced by passing sulphur dioxide into the solution. This sulphur dioxide was made by heating copper turnings with concentrated sulphuric acid and was purified from copper compounds mechanically carried along by passing through three gas washing-bottles, each containing a solution of sulphurous acid, and one column of beads moistened with a similar solution. From the solution of potassium and manganous sulphates the manganese was precipitated by the addition of an alkaline solution of ammonium carbonate. The manganous carbonate was washed with water until the washings were free from sulphates, then it was dissolved in nitric acid, which had been redistilled until free from chlorine, and the manganous nitrate was recrystallized six times from a solution strongly acid with nitric acid, four times in a glass vessel, twice in platinum. Usually it was necessary to start crystallization by inoculation, and cooling with ice was found advisable for the sake of economy in material. From a dilute solution of the purified nitrate in a platinum vessel, the manganese was again precipitated as carbonate, by means of ammonium carbonate which had been freshly made by passing pure carbon dioxide into distilled ammonia in a platinum flask. The resulting manganous carbonate, after thorough washing with water containing a small amount of ammonia to prevent colloidal

solution of the carbonate, was readily converted into bromide by solution in hydrobromic acid. Since it was probable that the carbonate contained occluded nitrate, and since a portion of the material had been oxidized to the manganic state during the washing, it was obvious that bromine would be set free during the solution in hydrobromic acid. The use of a platinum vessel for this purpose was therefore precluded. In order to avoid the introduction of silica, instead of glass vessels, quartz dishes were employed. These have been shown to be practically insoluble in acid solutions.<sup>1</sup> The free bromine was expelled from the solution of manganous bromide by prolonged heating on a steam-bath in a quartz dish. Finally it was crystallized six times, thrice in quartz, and, after filtration with a platinum funnel, thrice in platinum with centrifugal drainage after each crystallization. The crystals were dried as far as possible over stick potash in a vacuum desiccator. From the mother-liquors, by means of six similar crystallizations, Sample A<sub>2</sub> was obtained.

In the conversion of Sample B from permanganate to bromide minor changes were introduced. The ammonium carbonate was prepared in a pure state by distilling a solution of commercial ammonium carbonate in a platinum still. Instead of expelling free bromine from the solution of manganous bromide by prolonged heating upon the steam-bath, the solution was evaporated as far as possible upon the steam-bath and the residue was heated to 200° in an electric oven. The bromide was dissolved in water, and after filtration of the solution, was crystallized three times in a platinum dish. The third crop of crystals is designated as Sample C<sub>1</sub>.

Sample C<sub>1</sub> was prepared from a commercial specimen of pyrolusite. This was first dissolved in hydrochloric acid and the solution was boiled to expel chlorine. Hydrogen sulphide was passed into the diluted solution of manganous chloride to saturation, and the precipitate of sulphur and sulphides was removed by filtration. After the excess of hydrogen sulphide had been expelled by boiling, the solution was fractionally precipitated with sodium hydroxide until the precipitate was free from iron. Finally, the manganese was precipitated with ammonium carbonate and the precipitate was washed and dissolved in nitric

<sup>1</sup> Mylius and Meusser: *Z. anorg. Chem.* 44, 221 (1905). See also page 1565 of this paper.

acid. The nitrate was recrystallized and converted into bromide exactly as in the case of Sample A.

The source of Sample D was Merck's "chemically pure" manganous sulphate. A solution of 500 grams of this salt was first saturated with hydrogen sulphide, and the precipitate, which consisted chiefly of manganous sulphide, was removed by filtration. After the addition of a small amount of ammonia, hydrogen sulphide was again passed into the solution to saturation, and the precipitate discarded. In a similar way third and fourth fractions of sulphide were removed. Next the solution was thrice fractionated with small portions of potassium hydroxide, the precipitate being rejected in each case. Then the manganese was twice precipitated as carbonate by means of ammonium carbonate and the manganous carbonate was converted into bromide exactly as in the case of Sample B. The first crop of thrice recrystallized bromide is designated Sample D<sub>1</sub>, a second similar crop obtained from the mother-liquors is Sample D<sub>2</sub>.

*Manganous Chloride.*—Two samples of manganous chloride were prepared. Sample B corresponded in its purity to Sample B of manganous bromide, since both were made by dissolving the same specimen of manganous carbonate. The solution of the carbonate in hydrochloric acid, which had been distilled with a quartz condenser, was evaporated to dryness in a quartz dish and was heated to 200° in an electric oven. Then the filtered aqueous solution was evaporated to crystallization in a platinum dish and the first crop of crystals was twice recrystallized (Sample B<sub>1</sub>). The mother-liquors also yielded a crop of thrice recrystallized salt (Sample B<sub>2</sub>).

The mother-liquors of the manganous nitrate of Samples B and D were combined and recrystallized six times, three times in glass and three times in platinum, and from this pure nitrate Sample E<sub>1</sub> of manganous chloride was prepared as above.

*Hydrobromic Acid.*—Commercial bromine was freed from chlorine by twice converting the bromine into hydrobromic acid by means of thoroughly washed hydrogen sulphide and water, and heating the hydrobromic acid, after distillation, with recrystallized potassium permanganate. The bromine was thus twice distilled from a bromide, the bromide in the second distillation being almost free from chloride. Iodine was eliminated

by boiling the hydrobromic acid in each case with a small quantity of permanganate and rejecting the bromine set free. A portion of the final product, when converted into ammonium bromide by means of ammonia, and added to a solution of 3.46875 grams (in vacuum) of pure silver, yielded 6.03855 grams (in vacuum) of fused silver bromide, whence the ratio of silver to silver bromide is 57.443, while 57.445 is the value to be expected.<sup>1</sup>

By treating this bromine, covered with water, with washed hydrogen sulphide, hydrobromic acid was again produced. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was then filtered. In order to remove the sulphuric acid produced during the action of the bromine upon the hydrogen sulphide, the hydrobromic acid was first distilled. Then it was diluted, and a small quantity of recrystallized barium hydroxide was added to precipitate last traces of sulphuric acid. The slight precipitate of barium sulphate was collected upon a filter, and the acid was three times distilled with rejection of the first and last portions, with a glass retort and condenser. Finally the acid was once distilled with the use of a quartz condenser. The product of the final distillation was collected in quartz vessels and was used immediately for dissolving the manganous carbonate. That this acid was free from solid impurities, such as alkalies and silica, was shown by evaporating 30 cc. in a weighed platinum crucible. No weighable residue remained after the crucible had been heated to very dull redness.

*Hydrochloric Acid.*—The "chemically pure" acid was boiled for some time, after the addition of a small quantity of potassium permanganate. Then it was twice distilled in glass, the middle portion only being collected, and finally once in quartz shortly before use.

*Nitric Acid.*—This acid was twice distilled, all but the last third of the distillate being rejected in each distillation. This acid gave no test for chloride in a nephelometer.

*Silver.*—Five different specimens of silver were employed, a portion of each one of which had already been used in an atomic weight research, and had been shown to be of the highest grade of purity. Two of these specimens, Samples H and J, were used

<sup>1</sup> Baxter: "A Revision of the Atomic Weight of Bromine," *Pr. Am. Acad.* 42, 201 (1906).

in an investigation upon the atomic weight of iodine by one of us.<sup>1</sup> Sample H was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. Sample J was precipitated once as silver chloride, electrolyzed once, and finally precipitated with ammonium formate. Sample K was employed in our investigation upon the atomic weight of cadmium.<sup>2</sup> This sample was thrice precipitated as silver chloride and once electrolyzed. Sample L was precipitated once as chloride, once as metal by ammonium formate and was once electrolyzed. This sample has been used in the analysis of cadmium bromide.<sup>3</sup> Sample M was prepared for an investigation upon the atomic weight of bromine, and had been twice electrolyzed after a preliminary purification.<sup>4</sup> Samples H, J and L also were used in the latter research, and were found to give values identical with those obtained with sample M. All five samples were finally fused in a current of pure hydrogen in a lime boat. The fused lumps were cleaned with dilute nitric acid, cut into fragments either with a clean steel chisel and anvil, or with a jeweler's saw, treated with dilute nitric acid until free from iron, washed, dried, and finally heated to about 300° in a vacuum.

#### THE ANALYSIS OF MANGANOUS BROMIDE.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the halides, after fusion in hydrobromic or hydrochloric acid, were first titrated against weighed portions of pure silver. Then the precipitated silver salts were collected and weighed.

The apparatus used for the fusion of the manganous bromide in a current of nitrogen and hydrobromic acid gases, was used in the preparation of ferrous bromide by one of us,<sup>5</sup> and is a modification of apparatus used for a similar purpose in determinations of the atomic weights of cobalt,<sup>6</sup> nickel,<sup>7</sup> and uranium<sup>8</sup> in this labora-

<sup>1</sup> Baxter: *Pr. Am. Acad.* 41, 78 (1905).

<sup>2</sup> Baxter and Hines: *This Journal*, 27, 225 (1905).

<sup>3</sup> Baxter, Hines and Frevert: *Ibid.* 28, 770 (1906).

<sup>4</sup> Baxter: *Pr. Am. Acad.* 42, 207 (1906).

<sup>5</sup> Baxter: *Ibid.* 39, 246 (1903).

<sup>6</sup> Richards and Baxter: *Ibid.* 33, 117 (1897).

<sup>7</sup> Richards and Cushman: *Ibid.* 33, 99 (1897).

<sup>8</sup> Richards and Merigold: *Ibid.* 37, 378 (1902).

tory. A mixture of air and ammonia was passed over heated rolls of copper gauze and the excess of ammonia was removed by means of sulphuric acid. The gas was then purified and dried in an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers filled with granular fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through pure bromine in a small flask, passed into a second flask containing hydrobromic acid in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which, in the investigation upon ferrous bromide,<sup>1</sup> were found to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by resublimed phosphorus pentoxide.

The manganous bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen, purified as above and dried by phosphorus pentoxide, until the greater part of the crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by air which had been passed over solid potassium hydroxide, concentrated sulphuric acid and phosphorus pentoxide. As stated before, the purifying apparatus was constructed wholly of glass, in such a way that by means of stop-cocks any one gas or mixture of gases could be employed, to the exclusion of the others. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been frequently described in

<sup>1</sup> Loc. cit.

papers from this laboratory.<sup>1</sup> The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask and the salt was dissolved in about 300 cc. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited in a weighed porcelain crucible.

From the weight of manganous bromide very nearly the requisite quantity of pure silver could be calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering, in distilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent., and was slowly added with constant stirring to the 1 per cent. solution of manganous bromide in the precipitating flask. After having been shaken for some time, the solution was allowed to stand several days, one week in the case of Analyses 14 and 15, with occasional shaking, until the supernatant liquid was clear. Thirty cc. portions of the solution were then tested with hundredth-normal solutions of silver nitrate and sodium bromide in the nephelometer for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of silver bromide, otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about four centigrams of silver nitrate in excess were added to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible after it

<sup>1</sup> Richards and Parker: *Pr. Am. Acad.* 32, 59 (1896).



had been washed with water by decantation about ten times. Next it was heated for several hours at  $140^{\circ}$ , then for two hours at about  $230^{\circ}$  in an electric air-bath, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small crucible, contained in a large covered crucible, and again weighed. The fused salt was light yellow as a rule, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible together with a minute quantity of silver bromide which occasionally escaped the crucible, was collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of silver bromide. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions.

Several difficulties were met in carrying out the analyses. In the first place it proved difficult to wash the platinum boat absolutely clean. When rinsed with cold water only, and dried at  $100^{\circ}$ , the weight was in many cases a few hundredths of a milligram greater than before fusion of the bromide. Ignition to redness of the boat thus treated then produced a slight loss in weight. Rinsing with hot water reduced the gain in weight of the boat after drying but did not wholly prevent a slight loss on ignition. The cause of the variation was not discovered, hence it seems safer in the calculations to use the weight of the boat after drying. The total variation is so slight, however, that it scarcely affects the final result.

Two other difficulties arose from the fact that when a solution of a manganous salt, even as dilute as the filtrates from analyses, is filtered through filter-paper, in spite of long-continued washing a small amount of manganese is tenaciously retained by the paper. This was discovered from the fact that the asbestos residues always contained manganese. In Analyses 31 to 33 it was found possible to eliminate the manganese completely by washing the filter finally with 5 per cent. hydrobromic acid. In two cases (Analyses 29 and 30) the residues were analyzed for

manganese and were found to contain 0.00023 and 0.00057 gram of  $Mn_2O_4$  respectively.

The average of these two quantities is, however, larger than the total residue in some cases, hence this value can not be used to correct the previous analyses. In order to determine accurately the proper correction for this error, a solution containing manganous nitrate in the proportion in which it was usually contained in the filtrate of an analysis, was passed through filter-paper and the filters were then washed as thoroughly as possible with water. The ash of these papers invariably contained manganese, the weights of manganic oxide in several experiments being found to be 0.00018, 0.00011, 0.00006, 0.00018 and 0.00005 gram with an average of 0.00012 gram. This quantity was subtracted from the weight of asbestos shreds in all cases except Analyses 31 to 33, where the paper was washed with hydrobromic acid.

The residue obtained by the filtration of the manganous bromide proved to contain manganese and to be free from detectable amounts of platinum and silica. Probably this insoluble residue consisted chiefly of oxides of manganese, although prolonged fusion in hydrobromic acid failed to reduce materially the proportion of insoluble matter. The discovery of adsorption in the case of manganous nitrate led to the suspicion that at least a portion of this residue was due to adsorption of manganese compounds by the filter-paper. In order to test this point a solution of manganous bromide, containing about 5 grams in 200 cc., after one filtration was again filtered through a second filter about 3 cm. in diameter. Filters of this size were used in filtering the manganous bromide solution in the analyses. This filter was then washed with water as thoroughly as in an analysis, and was ignited. The weight of manganic oxide obtained was 0.00008 gram. Two repetitions of the experiment yielded 0.00008 and 0.00010 gram respectively. If, as is probable, the manganese is adsorbed, not as bromide, but as some basic compound, possibly as manganic hydroxide, the bromine would have remained partially, if not wholly, in the solution. In that case a suitable correction could be applied by subtracting from the weight of the residue the average of the quantities of manganese adsorbed in the above experiments. An attempt to prevent the difficulty by adding dilute sulphuric acid to the solution of manganous bromide

did not diminish the extent of the adsorption. Hence a negative correction of 0.00009 gram is applied to the residues in all cases.

#### THE ANALYSIS OF MANGANOUS CHLORIDE.

The apparatus employed for the fusion of manganous chloride was very similar to that used in the fusion of the bromide. Hydrochloric acid gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid. The gas was freed from spray in a gas washing-bottle, and was dried in five towers filled with beads moistened with concentrated freshly boiled sulphuric acid. From the towers the gas passed into the bottling apparatus in which the salt was fused in a current of hydrochloric acid and bottled in pure dry air as described above. This apparatus also was made wholly of glass with the exception of the air-drying towers which were closed with rubber stoppers. Since the salt was not heated in air no error could arise from this source.

In a few preliminary experiments the hydrochloric acid gas was passed finally over freshly sublimed phosphorus pentoxide, but this drying agent was subsequently eliminated since it was found to introduce volatile phosphorus compounds into the hydrochloric acid and thus into the manganous chloride, if the latter was moist. The effect of this difficulty upon previous work in this laboratory in the case of the analysis of chlorides which were fused in a current of hydrochloric acid gas, has been discussed elsewhere,<sup>1</sup> and has been shown to have been negligible. In the same place it has also been shown that hydrochloric acid gas attacks sulphuric acid to so slight an extent that the latter may safely be used to dry the former.

Although at first sight it is to be expected that hydrobromic acid, if dried by means of phosphorus pentoxide, would act upon this substance in a way similar to the action of hydrochloric acid gas, it has been shown<sup>2</sup> that no such difficulty exists if the hydrobromic acid is as dilute as in our work, the maximum concentration attainable by passing nitrogen through bromine at ordinary temperatures and then over phosphorus being not greater than 30 per cent. by volume.

The principal point of difference between the analyses of manganous bromide and manganous chloride was occasioned by the

<sup>1</sup> Baxter, Hines and Frevert: *This Journal*, 28, 779 (1906).

<sup>2</sup> *Ibid.* 28, 781 (1906).

greater solubility of silver chloride. This introduced no difficulty in the case of the titrations, although the opalescence in both nephelometer tubes was of course more marked at the end-point. In order to make the precipitation of the silver chloride more complete, however, a much larger excess of silver nitrate was necessary than in the case of silver bromide, about fifteen hundredths of a gram being added in each analysis. Furthermore, the precipitate was washed at first with a solution of silver nitrate containing four hundredths of a gram in a liter, although the final six washings were performed with water. The silver chloride dissolved in both filtrate and washings was determined by comparison as previously described. Here even the filtrate showed a trace of dissolved silver chloride.

In the case of manganous chloride also the extent of the adsorption of manganese compounds by the filter-paper was investigated by filtering a solution of the salt through a filter-paper, and, after thoroughly washing the paper, determining the residue after ignition. The correction for adsorption thus found, 0.00006 gram, is in some cases larger than the weight of the residue minus the loss in weight of the boat, owing possibly to the fact that not all the platinum lost by the boat is collected upon the filter-paper. At any rate the uncertainty introduced by applying the correction wherever possible is very small.

The filter upon which the asbestos shreds were collected was washed with warm dilute hydrochloric acid to eliminate adsorbed manganese compounds, so that no correction for adsorption is here necessary. This acid was then tested for silver chloride with the nephelometer, and if any was found it was added to the main weight of this substance.

In Analyses 32, 33, 34, 35 and 38 the silver nitrate was added to the manganous chloride, while in Analyses 36 and 37 precipitation was performed in the reverse fashion.

The possibility of the existence of manganic compounds in the salts was considered. In order to determine whether or not this was the case, one specimen of manganous chloride, after fusion in hydrochloric acid, was tested for manganic compounds by adding a solution of starch paste and potassium iodide. No coloration resulted even after the addition of hydrochloric acid, although a trace of permanganate produced immediate coloration in the same solution.

The fused salts were pink in the case of both the chloride and the bromide, hence Forchhammer's statement that the pink color of manganous salts is due to the presence of manganic compounds is incorrect.<sup>1</sup>

It has already been shown that chlorides and bromides which have been fused and allowed to solidify in an acid atmosphere occlude none of the gas, for they give neutral solutions.<sup>2</sup>

*The Nephelometer.*—The nephelometer employed for the estimation of slight opalescences has already been described in detail by Richards and Wells.<sup>3</sup> All the precautions necessary for the accurate use of this instrument were carefully observed. The two tubes to be compared were always of the same size. The source of light in the nephelometer was so adjusted that tubes containing exactly equal amounts of precipitate gave identical readings. It was found advantageous to insert a plate of ground glass between the source of light and the test-tubes. In making up the test solutions, great pains were taken that the concentration of electrolytes in the two solutions and the conditions of precipitation should be as nearly as possible the same. Final readings were taken only after the ratio between the two tubes had become constant.

*Vacuum Corrections.*—In order to find accurately the vacuum corrections for manganous bromide and chloride, it was necessary to determine the densities of these two salts. The experiments were carried out exactly as described in our determinations of the specific gravities of cadmium halides,<sup>4</sup> with the following results:

Density of $MnBr_2$ .		
Density of Toluene $25^\circ/4^\circ = 0.86156$ .		
Weight of $MnBr_2$ in vacuum. Grams.	Weight of toluene displaced in vacuum Gram	Density of $MnBr_2$ . $25^\circ/4^\circ$ .
3.0098	0.5914	4.385
3.0342	0.5963	4.384
		Average, 4.385

<sup>1</sup> Ann. Phil. N. S. 1, 50 (1821).

<sup>2</sup> Richards: Pr. Am. Acad. 29, 59 (1893); This Journal, 24, 376 (1902); Richards and Baxter: Pr. Am. Acad. 34, 367 (1899); Baxter and Hines: This Journal, 27, 227 (1905).

<sup>3</sup> Am. Ch. J. 31, 235 (1904); 35, 510 (1906).

<sup>4</sup> Ibid. 31, 220 (1904).

Density of $\text{MnCl}_2$ .		
Density of toluene $25^\circ/4^\circ = 0.86166$ .		
Weight of $\text{MnCl}_2$ in vacuum. Grams.	Weight of toluene displaced in vacuum. Gram.	Density of $\text{MnCl}_2$ . $25^\circ/4^\circ$ .
1.9436	0.5617	2.982
2.8532	0.8266	2.974
3.1202	0.9035	2.976
		Average, 2.977 <sup>1</sup>

All weights were reduced to the vacuum standard by applying the following corrections for each apparent gram of substance.

	Specific gravity.	Vacuum correction.
Weights.....	8.3	
$\text{MnBr}_2$ .....	4.385	+0.000129
$\text{MnCl}_2$ .....	2.977	+0.000259
$\text{AgBr}$ .....	6.473	+0.000041
$\text{AgCl}$ .....	5.56	+0.000071
$\text{Ag}$ .....	10.50	-0.000031
Toluene.....	0.862	+0.00126

The balance was a new Troemner, No. 10, and was easily sensitive to one-fiftieth of a milligram with a load of less than 50 grams. The weights, which were of brass, gold-plated, were occasionally carefully standardized to hundredths of a milligram. The corrections did not vary with time, however. All weighings were made by substitution, with tare vessels as nearly like those being weighed as possible.

The atomic weights involved in the calculations are assumed to be as follows:  $\text{Ag} = 107.930$ ;  $\text{Br} = 79.953$ ;<sup>2</sup>  $\text{Cl} = 35.473$ .<sup>3</sup>

Series I.	$\text{MnBr}_2 : 2\text{Ag}$ .....	54.959
" II.	$\text{MnBr}_2 : 2\text{AgBr}$ .....	54.955
" III.	$\text{MnCl}_2 : 2\text{Ag}$ .....	54.958
" IV.	$\text{MnCl}_2 : 2\text{AgCl}$ .....	54.958

Average, 54.958

The close agreement of the averages of the four series is conclusive evidence that no serious error, such as occlusion by the silver halides, affected the method of analysis. This is strikingly shown by the ratio between the silver used and the silver halide obtained in the same analysis.

<sup>1</sup> Shröder obtained the value 2.478. *Dichtigkeitsmessungen*, Heidelberg, 1873.

<sup>2</sup> Baxter: *Pr. Am. Acad.*, 42, 201 (1906).

<sup>3</sup> Richards and Wells: *Publications of the Carnegie Institution*, No. 28 (1905).



## THE ATOMIC WEIGHT OF MANGANESE.

MnBr<sub>2</sub> : 2AgBr.

Series II.

Ag = 107.930.

Br = 79.953.

Number of analysis	Sample of MnBr <sub>2</sub>	Weight of MnBr <sub>2</sub> in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of AgBr in vacuum Gram.	Loss on fusion. Gram.	Corrected weight of asbestos. Gram.	Weight of AgBr from which waters Gram.	Corrected weight of MnBr <sub>2</sub> . Grams.	Corrected weight of AgBr. Grams	Atomic weight of manganese.
16	A <sub>2</sub>	5.58461	0.00037	+0.00008	9.76524	0.00032	0.00069	0.00007	5.58416	9.76561	54.964
17	A <sub>2</sub>	5.63458	0.00022	+0.00004	9.85295	0.00030	0.00073	0.00007	5.63432	9.85345	54.961
18	A <sub>2</sub>	6.53738	0.00000	-0.00004	11.43246	0.00029	0.00078	0.00005	6.53738	11.43300	54.957
19	A <sub>1</sub>	4.81026	0.00019	+0.00002	8.41199	0.00024	0.00031	0.00006	4.81005	8.41206	54.959
20	C <sub>1</sub>	4.88124	0.00027	0.00000	8.53619	0.00022	0.00039	0.00006	4.88097	8.53642	54.980
21	C <sub>1</sub>	5.63234	0.00022	-0.00007	9.84971	0.00009	0.00046	0.00018	5.63219	9.85008	54.954
22	C <sub>1</sub>	6.52653	0.00017	+0.00010	11.41232	0.00018	0.00061	0.00005	6.52626	11.41293	54.958
23	A <sub>1</sub>	5.79927	0.00008	-0.00005	10.14153	0.00013	0.00061	0.00005	5.79924	10.14206	54.957
24	A <sub>1</sub>	3.59834	0.00015	+0.00010	6.29262	0.00014	0.00023	0.00004	3.59809	6.29271	54.952
25	B <sub>1</sub>	5.16345	0.00019	-0.00008	9.02941	0.00005	0.00023	0.00004	5.16334	9.02959	54.956
26	B <sub>1</sub>	3.92230	0.00014	-0.00010	6.85939	0.00012	0.00012	0.00041	3.92226	6.85968	54.951
27	B <sub>1</sub>	4.49181	0.00032	-0.00009	7.85527	0.00015	0.00059	0.00012	4.49158	7.85571	54.942
28	C <sub>1</sub>	3.60099	0.00016	+0.00012	6.29731	0.00014	0.00023	0.00007	3.60071	6.29740	54.949
29	D <sub>1</sub>	4.77414	0.00022	0.00000	8.34878	0.00020	0.00057	0.00046	4.77392	8.34915	54.951
30	D <sub>1</sub>	3.57674	0.00015	-0.00001	6.25541	0.00018	0.00046	0.00005	3.57660	6.25569	54.933
31	D <sub>2</sub>	5.69991	0.00026	-0.00007	9.96830	0.00020	0.00030	0.00005	5.69972	9.96840	54.947

Average, rejecting analysis 30, 54.955

Average of Series I and II, 54.957



### THE ATOMIC WEIGHT OF MANGANESE.

### Series III.

$$\text{MnCl}_2 : 2\text{Ag}.$$
$$Ag = 107.930.$$
$$C1 = 35.473.$$

Number of analysis.	Sample of $\text{MnCl}_2$ .	Sample Ag.	Weight of $\text{MnCl}_2$ in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $\text{MnCl}_2$ Grams.	Corrected weight of Ag. Grams.	Atomic weight of manganese.
32	$\text{B}_2$	L	4.62985	0.00017	-0.00002	7.93730	+0.00010	4.62970	7.93740	54.960
33	$\text{B}_1$	L	3.52899	.....	-0.00001	6.95071	-0.00030	3.52899	6.05041	54.958
34	$\text{B}_1$	L	3.30881	0.00000	-0.00010	5.67299	-0.00020	3.30881	5.67279	54.960
35	$\text{E}_1$	L	3.56859	0.00014	+0.00002	6.11818	0.00000	3.56843	6.11818	54.955
36	$\text{E}_1$	K	3.45114	0.00023	+0.00008	5.91647	-0.00010	3.45083	5.91637	54.958
37	$\text{B}_1$	L	4.47948	0.00008	-0.00015	7.68015	-0.00020	4.47948	7.67995	54.959
38	$\text{E}_1$	M	3.92089	0.00002	-0.00005	6.72232	-0.00005	3.92089	6.72227	54.958
									Average,	54.958

#### Series IV.

$$\text{MnCl}_2 : 2\text{AgCl}.$$
[illegible]

				Ag : AgBr.
Analyses	1	and	18.....	57.4438
"	2	"	19.....	57.4459
"	3	"	20.....	57.4426
"	4	"	21.....	57.4425
"	5	"	23.....	57.4439
"	8	"	24.....	57.4439
"	9	"	25.....	57.4457
"	10	"	26.....	57.4432
"	11	"	27.....	57.4423
"	12	"	28.....	57.4421
"	13	"	29.....	57.4454
"	14	"	30.....	57.4387
"	15	"	31.....	57.4456
				Average, 57.4435

Average, rejecting analyses 14 and 30, 57.4439

The most probable value for this ratio has recently been shown to be 57.4453.<sup>1</sup>

Richards and Wells have proved beyond question that the ratio of silver to silver chloride is as low as 75.2634,<sup>2</sup> a value which is identical with that obtained from the analysis of manganous chloride.

				Ag : AgCl.
Analyses	32	and	39.....	75.2615
"	33	"	40.....	75.2662
"	34	"	41.....	75.2628
"	35	"	42.....	75.2607
"	36	"	43.....	75.2595
"	37	"	44.....	75.2662
"	38	"	45.....	75.2656
				Average, 75.2632

It is interesting to tabulate the analyses according to the specimens of material employed.

Average of analyses with samples A <sub>1</sub> and A <sub>2</sub> of MnBr <sub>2</sub> ....				54.959
"	"	"	B <sub>1</sub>	.... 54.958
"	"	"	C <sub>1</sub>	.... 54.958
"	"	"	D <sub>1</sub> " D <sub>2</sub>	.... 54.951 <sup>3</sup>
"	"	"	B <sub>1</sub> " B <sub>2</sub>	MnCl <sub>2</sub> .... 54.960
"	"	"	E <sub>1</sub>	.... 54.956

Average, 54.957

<sup>1</sup> Baxter : Loc. cit.

<sup>2</sup> Loc. cit.

<sup>3</sup> Analysis 30 is rejected.

Average of analyses with sample H of Ag.....						54.958
"	"	"	"	"	J " "	54.961
"	"	"	"	"	K " "	54.959
"	"	"	"	"	L " "	54.959
"	"	"	"	"	M " "	54.958

Average, 54.959

The purification of Sample B was exceptionally thorough. In the first place potassium permanganate is isomorphous with a comparatively limited number of substances, so that the initial purification by a large number of crystallizations of this substance may be expected to have eliminated every trace of impurity of heavy metals. In the second place the final product had been many times recrystallized in the form of two other compounds of manganese. It is almost inconceivable that any impurity could have eluded this large number of crystallizations in three different forms. That such a prolonged purification was unnecessary is shown by the agreement of the results from the other samples with that from Sample B. Even in the case of Samples A, C, D and E the final product had been recrystallized in at least two forms. The slightly lower results in the case of Sample D differ from the others by an amount no greater than the possible experimental error, and can not be considered to indicate that the composition of this sample is different from that of the others.

The various samples of silver also yielded essentially the same result, which confirms the statement as to the identity of the different samples made on page 1566.

There can be little doubt that the final average of all four series, 54.96, represents with accuracy the relation of the atomic weight of manganese to that of silver 107.930. This value is in such close agreement with the value derived from previous investigations, that until the relation of oxygen to silver is more accurately known, no change in the atomic weight of manganese need be made from the value 55.0, now accepted by the International Committee on Atomic Weights.

The main results of this research may be briefly summarized as follows:

(1) The atomic weight of manganese, referred to silver 107.930, is found to be 54.96, by analysis of both manganous bromide and manganous chloride.

(2) The specific gravity of manganous bromide at 25°, referred

to water at  $4^{\circ}$ , is found to be 4.385, and that of manganous chloride under the same conditions is found to be 2.977.

We are deeply indebted to the Carnegie Institution of Washington for funds which have made this investigation possible, and also to Dr. Wolcott Gibbs and the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CHEMICAL LABORATORY OF HARVARD COLLEGE,  
CAMBRIDGE, MASS., July, 1906.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## A REVISION OF THE ATOMIC WEIGHT OF COBALT.

BY GREGORY PAUL BAXTER AND FLETCHER BARKER COFFIN.

Received August 13, 1906.

### FOURTH PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE.

SOME years ago the atomic weight of cobalt was investigated in this laboratory by the determination of the ratios of cobaltous bromide to silver and to silver bromide,<sup>1</sup> and of cobaltous bromide,<sup>2</sup> cobaltous chloride,<sup>3</sup> and cobaltous oxide<sup>3</sup> to cobalt. From these investigations the probable value for the atomic weight of cobalt was found to be 58.995 ( $Ag = 107.930$ ), the most satisfactory results being obtained through the analysis of cobaltous bromide.

The determination of the cobalt in cobaltous chloride was effected by reduction of the salt in a current of hydrogen. The salt was not obtained in a state of absolute purity, and it was necessary to apply corrections for the impurities, so that at the time very little value was attached to the result, 59.072.<sup>4</sup> In the present investigation it has been found possible with the help of the newly available quartz apparatus to prepare the salt in a state of greater purity, and the analysis of this new material confirms

<sup>1</sup> Richards and Baxter: *Pr. Am. Acad.* 33, 115 (1897).

<sup>2</sup> *Ibid.* 34, 351 (1899).

<sup>3</sup> *Ibid.* 35, 61 (1899).

<sup>4</sup> The value found from two analyses was 59.044, upon the assumption that the atomic weight of chlorine is 35.456 ( $Ag = 107.930$ ). Recent determinations in this laboratory by Richards and Wells (Publications of the Carnegie Institution, No. 28, 1905) have shown that the value of the latter constant is as high as 35.473. This change in the atomic weight of chlorine produces an increase in the atomic weight of cobalt of 0.028.

satisfactorily the previous analyses of cobaltous bromide, as well as the doubt concerning the earlier results with the chloride.

#### PURIFICATION OF MATERIALS.

*Cobaltous Chloride.*—The simplest method of freeing cobaltous salts from the salts of other metals was previously found to be precipitation of purpureo-cobalt chloride. This substance is only slightly soluble in cold hydrochloric acid solutions, but readily soluble in hot ammonia. It was prepared by bubbling air for several days through an ammoniacal solution of commercial cobalt chloride, and then adding hydrochloric acid in excess. The purpureo-chloride thus precipitated was collected and the mother-liquor removed as completely as possible by filtration upon a large porcelain Gooch crucible. It was then dissolved in hot redistilled ammonia, and the solution was filtered into a concentrated, distilled hydrochloric acid solution. The product, after washing with hydrochloric acid, was collected upon a Gooch crucible as before.

The final purification consisted in recrystallizing the amine three times by solution in the purest redistilled ammonia in a platinum dish, and filtration with a platinum funnel into a quartz dish containing hydrochloric acid which had been distilled with a quartz condenser. Care was taken always to have an excess of acid in the quartz dish, while the acid solution was never allowed to come in contact with platinum since it probably contained free chlorine. The product of the third precipitation was dried on a steam-bath, and was then converted into cobaltous and ammonium chlorides by heating to about  $200^{\circ}$  in a quartz crucible in an air-bath. For the latter purpose platinum proved to be unsuited, since it was slightly attacked during the decomposition of the amine, while the quartz crucible remained unchanged in weight. A temperature high enough to fuse the amine was very carefully avoided. The ammonium chloride still contained by the cobaltous chloride was eliminated during the final heating of the salt in a current of hydrochloric acid gas. During this final heating also care was taken to increase the heat very gradually, so as to avoid fusion of the salt and consequent possible enclosure of ammonium chloride in masses of fused cobaltous chloride.<sup>1</sup> Cobaltous chloride prepared in this way was designated Sample I.

<sup>1</sup> Z. physik. Chem. 46, 194 (1903).

For preparing the second sample of cobaltous chloride, cobalt-amine, which had been at least once dissolved in ammonia and reprecipitated with hydrochloric acid, was heated on a steam-bath with an excess of sulphuric acid, until all chlorine and hydrochloric acid had been expelled. The cobaltous sulphate thus formed was then dissolved in water, the solution was filtered and a large excess of ammonia was introduced. In order to free the cobalt from alkalis and silica this ammoniacal solution was then electrolyzed in a platinum dish, a platinum wire serving as anode, and the dish as cathode. The deposit of cobalt was washed thoroughly with pure water and dissolved in hydrochloric acid which had been freshly distilled through a quartz condenser. The solution was next evaporated to crystallization, and the product was twice recrystallized. In the third crystallization the salt was drained with a centrifugal machine in which platinum Gooch crucibles served as baskets and platinum crucibles as receivers. Any trace of sulphate occluded by the electrolytic metal was effectually eliminated in this way, for the mother-liquors from the second recrystallizations, when tested for sulphates, always yielded negative results.

After superficial moisture had been eliminated in a desiccator over potassium hydroxide, the salt was powdered in an agate mortar and heated in a platinum dish in an air-bath to expel the water of crystallization. The first molecules of water are lost below  $50^{\circ}$  and by keeping the temperature below this point it was possible to avoid melting the salt. It has been pointed out by Richards<sup>1</sup> that a salt dried in this way is left in the form of a skeleton which allows the escape of vapor from its inmost recesses, while if fusion takes place during drying, a portion of the original salt may be so enclosed within an impervious coating of anhydrous salt that escape of water is impossible. Except in Analyses 3 and 11 the remaining water of crystallization was expelled during the final heating of the cobaltous chloride in a stream of dry nitrogen and hydrochloric acid gases. Here also the temperature was at first so low that melting of the salt was completely avoided. The temperature was raised to  $400^{\circ}$  only after apparently all the water was expelled. In Analyses 3 and 11 all the water was expelled in the air-bath.

*Silver.*—Pure silver was prepared in the fashion usually em-

<sup>1</sup> Z. physik. Chem. 46, 194 (1903).

ployed in this laboratory as follows: To a dilute solution of silver nitrate an excess of hydrochloric acid was added. The silver chloride was shaken many times with pure water and was then reduced to metallic silver by means of a solution of sodium hydroxide and invert sugar. After the metal had been thoroughly washed with water, it was fused on charcoal with a blowpipe, and the lumps of silver were cleaned by scrubbing with sand and etching with nitric acid. Next they were dissolved in redistilled nitric acid, the excess of nitric acid was neutralized with redistilled ammonia, and the metal was precipitated with ammonium formate which had been made from redistilled formic acid. After the silver had been washed with pure water until free from ammonia, it was again fused in a boat of pure lime before a blowpipe. The buttons of silver were then cleaned with nitric acid and washed with water. Finally the silver was deposited electrolytically, the buttons in turn serving as the anode, a piece of the purest silver as the cathode, and a concentrated solution of one of the buttons in nitric acid as the electrolyte. The electrolytic crystals were washed with water and ammonia, dried, and fused in a boat of pure lime in a porcelain tube in a current of electrolytic hydrogen. The ingots were then cut into pieces of convenient size by means of a jeweler's saw, and were subjected to prolonged cleansing with successive portions of dilute nitric acid, until the acid no longer gave a test for iron, traces of which on the surface of the buttons had been introduced from the saw. The pieces were further cleaned with ammonia and with water, dried in air, and then heated to  $300^{\circ}$  and cooled in a vacuum. They were preserved in a desiccator containing solid potassium hydroxide.

#### METHOD OF ANALYSIS.

The cobaltous chloride, contained in a platinum boat, was first heated in a current of hydrochloric acid gas in a hard glass tube. An apparatus consisting of a series of towers which supplied either pure dry hydrochloric acid gas, nitrogen or air was constructed wholly of glass by Dr. M. A. Hines for work upon the atomic weights of cadmium<sup>1</sup> and manganese,<sup>2</sup> and was kindly loaned for this investigation. The hydrochloric acid gas was

<sup>1</sup> Baxter and Hines: This Journal, 27, 222 (1905); Baxter, Hines and Frevert: Ibid. 28, 770 (1906).

<sup>2</sup> Baxter and Hines: Ibid. 28, 1560 (1906).

generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and was dried by passing through five towers filled with beads moistened with concentrated sulphuric acid. Nitrogen was produced by passing a mixture of air with an excess of ammonia over heated rolls of copper gauze. It was freed from ammonia and further purified by passing through three wash-bottles containing dilute sulphuric acid, a tower filled with beads moistened with a solution of silver nitrate to remove sulphur compounds taken from rubber connections at the beginning of the apparatus, a tower filled with solid potassium hydroxide, then through three towers filled with beads moistened with concentrated sulphuric acid and finally through a tube containing resublimed phosphorus pentoxide. The air was purified by passing through a tower filled with solid potassium hydroxide, then through four towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube containing phosphorus pentoxide.

In preliminary experiments in which cobaltous chloride was fused in an atmosphere of pure hydrochloric acid gas, the platinum boat containing the salt was always seriously alloyed on the surface with metallic cobalt. This phenomenon was probably due to partial dissociation of the cobaltous chloride vapor which was invariably formed in considerable quantities when the salt was heated barely to fusion. It was possible to reach a temperature of  $400^{\circ}$  without meeting the above difficulty, consequently this temperature was employed in the preparation of all samples for analysis, although the salt was not fused at this temperature.

The salt was heated very gently at first in a current of hydrochloric acid gas containing a small quantity of nitrogen until the greater part of the ammonium chloride or water had been expelled, without melting the salt. Then the temperature was increased until finally the salt was maintained at about  $400^{\circ}$  for at least an hour, usually much longer. After the heating had ceased, the mixture of nitrogen and hydrochloric acid was displaced by nitrogen, and this in turn by dry air, and the boat was transferred to a weighing-bottle without exposure to moist air by means of the bottling apparatus which has frequently served



for a similar purpose in many atomic weight investigations in this laboratory.<sup>1</sup>

The weighing-bottle containing the boat and salt was weighed, after it had stood in a desiccator beside the balance case for some time. Then the boat was transferred to a flask containing about 250 cc. of pure water, and the weighing-bottle was rinsed with water, the rinsings being added to the solution in the flask. A trace of insoluble matter was collected by filtering the solution through a tiny filter into a glass-stoppered precipitating flask, and the filter was ignited in a weighed platinum crucible. This residue, which consisted chiefly of cobalt oxide, never amounted to as much as two-tenths of a milligram. In Analyses 1, 2, 9 and 10 a slight increase in the weight of the boat was caused by incipient dissociation of the salt and alloying of the boat. The increase was only 0.05 mg. in the case of Analyses 1 and 9, 0.66 mg. in the case of Analyses 2 and 10. In these cases the weight of the boat after solution of the cobaltous chloride in water, washing and drying at 100° was determined and used in the calculations. These two analyses yielded results essentially identical with the remainder.

From the corrected weight of cobaltous chloride very nearly the requisite quantity of pure silver was calculated. This silver was weighed out, and dissolved in redistilled nitric acid diluted with an equal volume of water in a small flask provided with a column of bulbs to prevent loss by spattering. After the solution had been diluted with an equal volume of water, the nitrous fumes were expelled by gentle heat. Then the solution of silver nitrate, after dilution until its concentration was about 1 per cent., was poured slowly, with constant agitation, into the solution of cobaltous chloride, which also had been diluted to a like concentration in the precipitating flask, and the flask was shaken for some time. The precipitation and subsequent filtration of the silver chloride were carried out in a cupboard made of ruby glass.

After the solution had stood for about two days with occasional agitation, and after the supernatant liquid had become perfectly clear, 25 cc. portions of the solution were tested with hundredth-normal solutions of silver nitrate and potassium chloride in a

<sup>1</sup> Richards and Parker: *Pr. Am. Acad.* 32, 59 (1896).

nephelometer<sup>1</sup> for excess of chloride or silver, and, if necessary, either standard silver nitrate or potassium chloride solution was added, and the process of shaking and testing repeated, until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask since they contained an appreciable amount of silver chloride and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced.

As soon as the exact end-point had been found, about one decigram of silver nitrate in excess was added, in order to produce as complete precipitation of the silver chloride as possible, and the flask was again shaken and allowed to stand until clear. The precipitate of silver chloride was collected upon a Gooch crucible, after it had been washed several times with a dilute solution of silver nitrate and finally ten times with pure water. Then it was heated in an electric oven for five hours at 180°, cooled in a desiccator and weighed.

In order to determine the moisture still retained by the dried silver chloride, in each case it was transferred as completely as possible to a porcelain crucible and weighed. Then the salt was fused by heating the small covered crucible contained in a large crucible and again weighed.

Although the filtrate and silver nitrate wash-waters were nearly free from dissolved silver chloride, the aqueous washings contained appreciable quantities of this substance. The amount of dissolved salt in both filtrate and wash-waters was determined by comparison with standard chloride solutions in a nephelometer. It has recently been found in this laboratory by Richards and Stähler that if the solution is made slightly alkaline with ammonia and then is acidified immediately before being tested, more accurate results are obtained.<sup>2</sup> This procedure was followed in the greater part of our analyses. The testing took place very shortly after the filtration, so that suspended material had no time to settle.

After the filtrate and wash-waters had been analyzed for dissolved silver chloride, they were filtered through a tiny filter to collect a small quantity of asbestos mechanically detached from the Gooch crucible. This filter was washed with ammonia to

<sup>1</sup> Richards and Wells : *Am. Ch. J.* 31, 220 (1904).

<sup>2</sup> *Ibid.* 35, 512 (1906).

eliminate the silver chloride, which might have been collected and which had been determined in the nephelometric test, and was ignited in a weighed platinum crucible.

For most of the work a new short-armed Troemner balance, sensitive to a fiftieth of a milligram with a load of 50 grams, was used. The gold-plated brass weights were three times carefully standardized to hundredths of a milligram and were used for no other work. Weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible.

In order that the proper vacuum correction for cobaltous chloride might be applied, the density of this substance was determined by Dr. M. A. Hines in connection with similar work upon manganese. The salt was first fused in a platinum boat in a current of hydrochloric acid gas, and then the toluene displaced was determined with a pycnometer previously described.<sup>1</sup>

Density of  $\text{CoCl}_2$ .

Density of Toluene = 0.86166.

Weight of $\text{CoCl}_2$ in vacuum Grams	Weight of toluene displaced in vacuum. Grams	Density of $\text{CoCl}_2$ . $25^\circ/4^\circ$
4.8719	1.2522	3.352
4.6520	1.1991	3.343
		Average, 3.348 <sup>2</sup>

The following vacuum corrections were applied: Cobaltous chloride, +0.000215; silver, —0.000029; silver chloride, +0.000073.

Evidence of the purity of the silver and of the absence of appreciable occlusion by the silver chloride may be obtained from the relation between the amount of silver used in the titrations and the corresponding amount of silver chloride formed. In all, 29.46524 grams of silver produced 39.14905 grams of silver chloride, a ratio of 100.000 to 132.865. Richards and Wells found this ratio to be 100.000 to 132.867.

Attention should be called to the fact that if the salt made from the amine still contained appreciable amounts of ammonium chloride after being heated, the observed value for the atomic weight of cobalt would have been too low. On the other hand, if the cobaltous chloride made from the crystallized salt retained traces of water, the result would have been too high. The average

<sup>1</sup> Baxter and Hines: *Am. Ch. J.* 31, 220 (1904).

<sup>2</sup> Playfair and Joule obtained the value 2.937. Landolt-Bornstein: *Physikalisch-Chemische Tabellen*, 3rd Ed., p. 238.



of all the results obtained with salt made from the amine is 58.995, and the average of the results with salt made from the crystallized chloride is 58.998. The very slight difference between these values lies within the experimental error of the determinations. Evidently, the salt was in all cases essentially free both from ammonium chloride and water. The almost complete absence of ammonium chloride was also shown by two experiments in which the amine was heated in a current of hydrochloric acid in the usual manner, and then the salt was dissolved in water and the cobalt was precipitated by the addition of ammonia-free sodium hydroxide. In one case where 1.76 grams of cobaltous chloride were used, the filtered solution, when tested with Nessler's reagent, showed the presence of 0.00025 gram of ammonium chloride, while in the other 2.13 grams of cobaltous chloride yielded 0.00005 gram of ammonium chloride. This proportion of impurity would have lowered the observed atomic weight 0.004 in the first case, and only 0.001 in the second. The average 0.003 is exactly the difference between the averages from the two samples of material. If this correction is applied in the analyses where the cobaltamine was used, the averages of both Series I and Series II are raised to 58.998, a negligible change.

Whether or not such a correction is applied the average of Series I and II confirms very closely the value 58.995 previously found by analysis of the bromide, hence the atomic weight of cobalt may, as before, be assumed to be 59.00 referred to silver 107.930.

We are deeply indebted to the Cyrus M. Warren Fund for Research in Harvard University for many platinum, quartz, and other vessels.

CAMBRIDGE, MASS.,  
August 10, 1906.

## SEPARATION AND ESTIMATION OF BERYLLIUM.

BY CHARLES L. PARSONS AND S. K. BARNES.

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THE separation of beryllium from other elements presents little difficulty except in the case of aluminum and iron. It will invariably be found with aluminum in the last instance, and the problem therefore becomes the determination of beryllium in such a mixture.

Many methods for the separation of beryllium from iron and aluminum have been proposed but the one most often used has been founded upon the solubility of its hydroxide in ammonium carbonate which unfortunately dissolves also some of the hydroxides of aluminum and iron. Vauquelin<sup>1</sup> in 1798 first used ammonium carbonate, but his first separation depended upon the solubility of beryllium hydroxide in potassium hydroxide and its precipitation on boiling. Gmelin<sup>2</sup> and Schaffgotsch<sup>3</sup> both used this same method but it is very far from being accurate. Scheerer<sup>4</sup> first proposed the separation of the last traces of iron from the ammonium carbonate solution by means of ammonium sulphide. Berthier<sup>5</sup> suggested the use of ammonium sulphite as a reagent but the method was shown to be valueless by Bottinger.<sup>6</sup> In 1850 Rivot<sup>7</sup> proposed the ignition of the oxides in a current of hydrogen whereby the iron was reduced to metal and could be dissolved out with dilute nitric acid or its mass determined by the loss of weight. Debray<sup>8</sup> developed a separation dependent upon the action of zinc on the mixed sulphates precipitating the aluminum as a basic sulphate, but the method was never made quantitative. Joy<sup>9</sup> made a comparative study of all methods proposed to his time. Gibbs,<sup>10</sup> in 1864 for the first time, suggests the use of sodium fluoride to quantitatively separate aluminum from beryllium, and Pollok<sup>11</sup> shows that the fluoride separation is exceedingly sharp. Cooke,<sup>12</sup> after reducing the iron in hydrogen, volatilizes it in a current of hydrochloric acid. Havens and Way<sup>13</sup> accomplish the same result without previous reduction of the oxide. Rössler<sup>14</sup> succeeded in separating beryllium from small amounts of aluminum by precipitating with ammonium

<sup>1</sup> Ann. chim. phys. 26, 155.

<sup>2</sup> Ann. Physik. 50, 175.

<sup>3</sup> Ibid. 50, 183.

<sup>4</sup> Ibid. 56, 479.

<sup>5</sup> Ann. chim. phys. [3] 7, 74.

<sup>6</sup> Ann. 51, 397.

<sup>7</sup> Ann. chim. phys. [3] 30, 188.

<sup>8</sup> Ibid. [3] 44, 1.

<sup>9</sup> Am. J. Sci. [2] 36, 83.

<sup>10</sup> Ibid. [2] 37, 346.

<sup>11</sup> Trans. Roy. Dublin Soc. [2] 1904, 139.

<sup>12</sup> Am. J. Sci. [2] 42, 78.

<sup>13</sup> Ibid. [4] 8, 217.

<sup>14</sup> Z. anal. Chem. 17, 148.

phosphate in the presence of citric acid. Vincent<sup>1</sup> uses dimethylamine to precipitate beryllium salts and finds that the aluminum compound is soluble in excess of the reagent. Iron acts like beryllium. Renz<sup>2</sup> confirms this, states the same to be true of methyl-, ethyl- and diethylamine, and claims the results to be quantitatively accurate. Zimmermann<sup>3</sup> in 1887 returns to the old potassium hydroxide and sulphite or thiosulphate method without any special addition. Scheier<sup>4</sup> in 1892, Atkinson and Smith<sup>5</sup> in 1895 and Burgass<sup>6</sup> in 1896 separate iron quantitatively from beryllium by means of nitroso- $\beta$ -naphthol. Lebeau<sup>7</sup> precipitates the iron in nitric acid solution by ferrocyanide, removes the ferrocyanide by copper nitrate and the excess of copper by hydrogen sulphide. Hart<sup>8</sup> removes the major part of both iron and aluminum by careful precipitation of the sulphates with sodium carbonate, the beryllium being the last to precipitate, owing to the great solubility of its own hydroxide in its own sulphate. Havens<sup>9</sup> separates beryllium from aluminum quantitatively by the insolubility of hydrous aluminum chloride in a mixture of hydrochloric acid and ether which has been saturated with hydrochloric acid gas. Haber and Van Oordt<sup>10</sup> dissolve basic beryllium acetate in chloroform, leaving aluminum and iron acetates behind. Myers<sup>11</sup> removes iron electrolytically from a slightly acid solution of the sulphates, using a mercury cathode. Parsons and Robinson<sup>12</sup> separate beryllium basic acetate in a pure state from other acetates by means of its ready solubility in hot glacial acetic acid and comparative insolubility in the same reagent when cold.

#### PRELIMINARY INVESTIGATIONS.

Some qualitative work done by one of us some months ago had developed the fact that beryllium hydroxide was readily, im-

<sup>1</sup> Bull. soc. chim. 33, 157.

<sup>2</sup> Ber. 36, 2751.

<sup>3</sup> Z. anorg. Chem. 15, 285.

<sup>4</sup> Chem. Ztg. 16, 420.

<sup>5</sup> This Journal, 17, 688.

<sup>6</sup> Z. angew. Chem. 1896, 596.

<sup>7</sup> Compt. rend. 121, 641.

<sup>8</sup> This Journal, 17, 604.

<sup>9</sup> Am. J. Sci. [4] 4, 111.

<sup>10</sup> Z. anorg. Chem. 40, 465.

<sup>11</sup> This Journal, 26, 1124.

<sup>12</sup> Ibid. 28, 555.

mediately and apparently completely separated from aluminum and ferric hydroxides by boiling momentarily in a saturated solution of acid sodium carbonate. No trace of aluminum could be found in the separated beryllium compound by Haven's method<sup>1</sup> and the white hydroxide of beryllium or its hydrochloric acid solution showed scarcely a trace of color. The object of this investigation was to determine whether or not this reaction could be made strictly quantitative.

Solutions of pure aluminum chloride and pure beryllium chloride were made and analyzed, and it was early apparent on attempting to get closely agreeing results by precipitating the beryllium as hydroxide with ammonia that some source of error existed. After some experimenting it was found that the beryllium hydroxide, when freed of the ammonium chloride present, passed into the colloidal condition on washing with pure water and indeed much more rapidly than is known to be the case with aluminum. On adding a small amount of ammonium acetate to the wash-water the difficulty immediately disappeared and no trouble was experienced in obtaining well-agreeing results even in fairly strongly ammoniacal solution. Small amounts of beryllium hydroxide also adhere tenaciously to the glass of the precipitating beaker and after as perfect mechanical removal as possible the beaker should be treated with a little dilute nitric acid and the contained beryllium reprecipitated. Beryllium oxide obtained by blasting the hydroxide is somewhat hygroscopic and should be weighed with due precautions.

#### SEPARATION AND DETERMINATION.

The method is based on the total insolubility of aluminum and ferric hydroxide in a 10 per cent. boiling acid sodium carbonate solution and on the total solubility of beryllium hydroxide in the same. From the aluminum solution used the aluminum hydroxide was totally precipitated by the boiling hot saturated solution of acid sodium carbonate and the beryllium solution gave a perfectly clear solution with the same. The acid sodium carbonate employed was in the form of small crystals and contained but a trace of the normal carbonate as indicated by phenolphthalein.

Portions of the solutions of beryllium and aluminum chlorides were weighed out containing amounts convenient to work with,

<sup>1</sup> Loc. cit.



and washed from the weighing-bottle into clean Jena beakers of 250 cc. capacity in which the separation was made.

The solution was made up to about 100 cc., neutralized as nearly as possible with ammonia and 10 grams of solid acid sodium carbonate added. If the solid carbonate is added to any but a cold solution spattering will take place.

The beakers were kept covered with watch-glasses to prevent loss of material by any escaping gas during the heating and the solution was brought to a boil as quickly as possible and allowed to boil not to exceed one minute. Carbon dioxide is not evolved very rapidly till the boiling temperature is nearly reached if the solutions are neutral, but evolution of gas must not be mistaken for boiling.

The solution was now set in cold water and cooled, filtered and washed two or three times with hot water. The precipitate was dissolved on the filter with as little as possible (1:1) hydrochloric acid and run back into the same beaker in which the precipitation was first made, the solution made up to 100 cc., made neutral with ammonia, precipitated again with acid sodium carbonate as before, cooled, filtered and washed with hot water, running both filtrates together. A cloudiness will be noticed in the combined filtrates after washing, which looks as if aluminum hydroxide were coming through but this is not the case, the cloudiness being due to the dilution of the strong acid sodium carbonate solution with water. The aluminum hydroxide was again dissolved in (1:1) hydrochloric acid, precipitated with ammonia and determined in the ordinary way, as it was found that it was next to impossible to wash out all the acid sodium carbonate from the gelatinous precipitate.

The filtrate from the double precipitation, containing the beryllium in solution, was carefully acidified with strong hydrochloric acid in a covered beaker as special care was required that the escaping gas should not cause mechanical loss. Just before neutralization a portion of the beryllium was thrown down as hydroxide but this immediately dissolved on addition of more acid. The solution was then boiled to remove carbon dioxide so that no ammonium carbonate should be formed, precipitated with ammonia, boiled, allowed to settle and filtered, washing with ammonium acetate solution until free from chlorides. The

beryllium hydroxide was ignited to constant weight, which is readily attained, and weighed.

Results follow:

Al <sub>2</sub> O <sub>3</sub>		BeO.		Total	
Taken	Found	Taken.	Found.	Taken.	Found.
0.1252	0.1266	0.0818	0.0810	0.2070	0.2076
0.1323	0.1336	0.0795	0.0781	0.2118	0.2117
0.0942	0.0957	0.0573	0.0563	0.1515	0.1520
0.0869	0.0881	0.0610	0.0588	0.1479	0.1469
0.0907	0.0945	0.0629	0.0594	0.1536	0.1539

The results are slightly too high in aluminum oxide and correspondingly low in beryllium oxide although the totals found agree closely with the theoretical amounts. The aluminum hydroxide showed therefore, as was to be expected, a tendency to occlude some beryllium hydroxide. Washing the first and second precipitation with hot acid sodium carbonate solution was next tried and this seemed to assist in removing the beryllium, although small amounts were still left behind in the aluminum hydroxide as the following results will show.

Al <sub>2</sub> O <sub>3</sub>		BeO		Total	
Taken.	Found	Taken	Found	Taken	Found.
0.0840	0.0849	0.0646	0.0642	0.1486	0.1491
0.0740	0.0749	0.0680	0.0676	0.1420	0.1425
0.2059	0.2055	0.0972	0.0977	0.3031	0.3032
0.6152	0.6167	0.0372	0.0348	0.6524	0.6515
0.1327	0.1346	0.3125	0.3107	0.4452	0.4453
0.1368	0.1386	0.3050	0.3031	0.4418	0.4417
0.6233	0.6250	0.0730	0.0714	0.6963	0.6964

Trials were made of heating the acid sodium carbonate solution in pressure flasks so that no carbon dioxide might escape, but the results were not satisfactory.

By the procedure so far followed the mixed hydroxides were first precipitated together in the cold and the beryllium hydroxide dissolved in the boiling reagent. This would seemingly tend to allow the aluminum hydroxide to so enclose some of the solid beryllium hydroxide that the reagent could not act upon it. This was particularly the case when relatively large amounts of aluminum were present. To overcome this difficulty as much as possible, separations were tried by adding the boiling hot mixture of the chlorides to a nearly boiling solution of acid sodium carbonate containing enough of the reagent to make the mixed liquid an approximately 10 per cent. solution. The whole was then brought to a boil, held there for half a minute, cooled and treated

as before. By this procedure only the aluminum was precipitated as hydroxide and less beryllium was mechanically retained. Larger amounts of aluminum were used in this case than before and as the results could be interpreted from the beryllium alone the aluminum was not weighed.

BeO	
Taken.	Found.
0.1311	0.1307
0.1424	0.1415
0.2522	0.2515
0.0671	0.0664
0.0642	0.0631

To show the application of this same procedure in the presence of iron, ferric chloride was added in variable amounts, both large and small, to mixtures of aluminum and beryllium chlorides, boiled with a little nitric acid to insure oxidation and the whole treated as above. The combined hydroxides of iron and aluminum were several times the mass of the beryllium hydroxide yet the separation was almost complete and the resulting beryllium oxide was analytically pure.

BeO	
Taken.	Found.
0.2152	0.2146
0.0911	0.0906
0.0825	0.0806
0.1020	0.0995

Considering the well-known great tendency of gelatinous hydroxides like those of aluminum and iron to retain other substances which may be present, this separation of beryllium leaves little to be desired. Care must, of course, be exercised to bring the acid sodium carbonate quickly to a boil and to boil for a moment only, for if too much carbon dioxide is lost the aluminum may partially pass into solution.

#### CONCLUSIONS.

Beryllium hydroxide must be washed with water containing an electrolyte to prevent the loss of colloidal hydrate through the filter.

Beryllium can be quantitatively separated from iron and aluminum by means of the solubility of its hydroxide in a boiling hot solution of acid sodium carbonate of approximately 10 per cent. strength.

## THE DETECTION OF BARIUM, STRONTIUM AND CALCIUM.

BY STANLEY R. BENEDICT.

Received August 30, 1906

THE distinctive features of the following method for the detection of the alkaline earth metals may be briefly summarized as follows: (1) In contradistinction to most, if not all other, methods, it provides for the removal of barium without the use of chromate or dichromate, thus giving colorless solutions for the subsequent detection of strontium and calcium. (2) It entirely avoids the somewhat troublesome operation of filtering solutions containing the precipitated sulphates of calcium, barium or strontium. (3) The method is very rapid, the manipulation simple, and the results positive. The precipitates dealt with filter perfectly clear without difficulty.

The reagents used are saturated potassium iodate solution, dilute hydrochloric acid, ammonium oxalate, and saturated ammonium sulphate solution.

As preliminary to an outline of the method, it may be well to mention the following facts, upon which it is based.

Barium iodate, while somewhat soluble in water, is practically insoluble in an excess of potassium iodate solution of proper concentration, even in the presence of a certain amount of hydrochloric acid. Barium is therefore completely precipitated from its solutions by an excess of potassium iodate, in presence or absence of dilute hydrochloric acid, the filtrate yielding absolutely no turbidity with sulphate or chromate solutions.

Strontium iodate is more soluble in water than is the corresponding barium compound. Like the barium salt it is completely precipitated from neutral or slightly ammoniacal solutions upon addition of a considerable amount of iodate solution, the precipitation taking place somewhat more slowly than with the barium compound. Unlike the barium salt however, strontium iodate is quite soluble in dilute hydrochloric acid, and strontium is therefore only incompletely, if at all, precipitated by an iodate from its solutions which have been acidified with dilute hydrochloric acid.

Calcium iodate is more soluble than either the barium or strontium compound, and is only incompletely, if at all, precipitated from neutral, acid or ammoniacal solutions, upon addition of an excess of iodate solution.

The precipitated iodates of all these metals form bulky, granular precipitates which filter clear very rapidly.

An outline for the procedure for the identification of calcium, strontium and barium follows.

A portion (2-3 cc.) of the solution to be tested is acidified with one-half its volume of 5N hydrochloric acid, and to the liquid thus obtained, its own volume of a saturated solution of potassium iodate is added. If a precipitate forms *at once*, barium is present. If no precipitate forms, barium is absent. If a precipitate forms slowly, either barium is present in low concentration or strontium is present in considerable amount. In such a case the presence or absence of barium should be confirmed by the addition of a few drops of dichromate solution to the original solution. This confirmation is rarely necessary.

Having established the presence or absence of barium, the solution is agitated and allowed to stand for one-quarter to one-half a minute. The precipitate is filtered off, and to a portion of the filtrate (not the first portion through the filter) is added a little more than an equal volume of a saturated solution of ammonium sulphate. The solution is then heated to boiling. A white precipitate, permanent on boiling, consists of strontium sulphate and indicates strontium.

To another portion of the original solution is added two volumes of a saturated potassium iodate solution, the mixture agitated and allowed to stand one-half to one minute and filtered. To the filtrate is added some ammonium oxalate solution (one-half volume of the ordinary reagent). The solution is now warmed to boiling. The formation of a white precipitate (consisting of calcium oxalate), either in the cold or upon warming, indicates calcium.

The directions given above apply to neutral or faintly ammoniacal solutions of the chlorides of calcium, strontium and barium. In the ordinary course of a qualitative analysis the precipitated carbonates should be dissolved in a little hydrochloric acid and the resulting solution evaporated to dryness, warming gently to expel free acid. The residue from this evaporation should be

dissolved in 6 to 10 cc. of water, and this solution used for the analysis. The portion to be tested for calcium may be treated with a drop of ammonium hydroxide solution to insure the absence of free acid.

In the use of the above method, particular attention should be given to the following points: The potassium iodate solution used as a reagent must be fully saturated. This reagent is conveniently prepared by using enough of the dry salt to make a  $N/2$  solution and allowing it to stand some hours, with occasional shaking. If it is desired to dissolve the salt more quickly by heating to boiling, the warm solution must be cooled to ordinary temperature and agitated before use.

In adding the reagents, particularly the iodate and hydrochloric acid solutions, the amounts added must correspond quite closely with what is called for in the directions given above. The adequacy of these directions has been tested by their employment in analyses of some forty mixtures by myself and others, in the laboratory of the University of Cincinnati. The results obtained were entirely correct.

I desire to express my sincere thanks to Dr. J. F. Snell, whose continued encouragement and suggestions have been invaluable, in this, as in my previously published work.

## THE DETERMINATION OF TOTAL ARSENIC ACID IN LONDON PURPLE.

BY EDWARD G. MAHIN.

Received August 30, 1906.

MOST methods now in use for the determination of arsenic acid, present, when applied to London purple, certain serious difficulties, to avoid which was the object of the work outlined in the present paper. The Association of Official Agricultural Chemists recommends the method stated briefly as follows:<sup>1</sup>

Two grams of the sample are dissolved in 80 cc. of water and 20 cc. of hydrochloric acid at about  $70^{\circ}$ , one-sixth of this solution is treated with 50 cc. of hydrochloric acid and 3 grams of potassium iodide and allowed to stand, by which means all of the arsenic is reduced to the state of arsenious acid. The free iodine is removed by the addition of  $N/10$  sodium thiosulphate; the

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., Cir. 10, p. 4.

solution is now made alkaline with solid sodium carbonate, the excess of this removed by means of hydrochloric acid, and then sufficient solid sodium bicarbonate added to make the solution decidedly alkaline. The solution is then titrated with standard iodine solution. Total arsenious acid having been determined in a similar manner, omitting the reduction by hydriodic acid, the total arsenic acid is calculated by difference.

The presence of the large amount of purple dye which is always found in London purple is not particularly objectionable to the practiced operator when titrating in basic solution with iodine, but in strongly acid solution, such as is present during the reduction of arsenic acid, it becomes practically impossible to determine when the iodine, liberated by the action of arsenic acid upon hydriodic acid, is exactly used up by the sodium thiosulphate, even by the use of the outside testing method recommended by the association. Davidson<sup>1</sup> directs that a part of the dye be precipitated by the addition of sodium carbonate, the solution filtered and an aliquot portion be treated with hydrochloric acid and potassium iodide. This is certainly an improvement but is, in the opinion of the writer, far from being a completely satisfactory method, inasmuch as a considerable portion of the dye remains in solution, even after this treatment.

Since the arsenic is eventually all brought to the lower state of oxidation and any intermediate oxidation or reduction should occasion no error in the determination, it seemed possible that the solution might be successfully bleached by chlorine and all interfering dye destroyed. This point was investigated, with results which will appear later.

The neutralization of a considerable amount of hydrochloric acid by means of powdered sodium carbonate is a quite tedious operation in this case, not only on account of the tendency of the carbonate to form lumps in the solution, these acting only slowly upon the acid, but also because an excess of sodium carbonate must be avoided on account of the later use of iodine. Since the acid becomes very dilute toward the last, the action becomes correspondingly slow from this cause. The formation of lumps may be partially avoided by the use of the crystalline form of sodium carbonate, but in any case the slow addition of a rather large quantity is necessary and the bicarbonate must be added later.

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., Bull. 99, p. 27.

It was thought possible that the amount of acid used, consequently the amount of carbonate required, was unnecessarily large in both methods, also that a calculated amount of sodium bicarbonate might be substituted for the normal carbonate, adding the former as rapidly as could be done without danger of loss by frothing, in this way providing a large surface for the action of the acid when the latter becomes dilute.

Experimental work was undertaken in order to determine the measure of accuracy of a method involving the changes suggested above, with results which follow.

Chlorine, evolved by the action of potassium permanganate upon concentrated hydrochloric acid, and passed into the warm semi-solution of London purple in hydrochloric acid, produces in less than ten minutes a brown precipitate of organic matter which, after removal by filtration, leaves a slightly yellow solution in which the titration of iodine with sodium thiosulphate and of arsenic with iodine is easily accomplished. The presence of chlorine in the solution and the fact that all of the arsenic is in the oxidized form necessitate, of course, the presence of a somewhat larger quantity of potassium iodide.

The amount of acid added to the aliquot part of the solution in which the arsenic acid is to be reduced was changed from the 50 cc. of the official method or the 25 cc. of Davidson's modification, to 10 cc. The reduction of arsenic acid is, as might be expected, not complete at the moment of the addition of hydrochloric acid and potassium iodide, nor does this reduction proceed as rapidly during the addition of sodium thiosulphate as is the case with larger amounts of acid, but it was found that the reaction was sufficiently rapid to serve the purpose and, since one of the products (iodine) is removed to practical completion, the reaction is quantitative.

Powdered sodium bicarbonate was substituted for the normal carbonate, using a weight calculated to leave an excess of from 3 to 5 grams after the neutralization of all of the acid. Although this causes a more copious evolution of carbon dioxide, it was found possible to complete the addition in less time than was the case with the normal carbonate, for reasons already mentioned.

The method finally used for total arsenic acid is as follows: Warm 4 grams of London purple, 40 cc. of concentrated hydrochloric acid, and 150 cc. of water to not over 80° in a 250 cc.



flask, until the soluble portion has dissolved. Immediately pass in a rapid stream of chlorine for ten minutes; transfer to a 500 cc. graduated flask, dilute to the mark with cold water, and mix. Filter through a folded filter, rejecting the first 30 to 50 cc. Measure 50 cc. of the nearly colorless solution into a 500 cc. Erlenmeyer flask, add 10 cc. of concentrated hydrochloric acid and warm to  $80^{\circ}$  on the water-bath, then add 5 grams of potassium iodide and allow to stand for ten minutes. At the end of this period add sodium thiosulphate (about N/20) from a burette until the iodine is exactly removed. It is best to avoid the addition of starch solution at this point, on account of the deep red color which is produced by the action of iodine upon dextrin, the latter being almost invariably present or formed in strongly acid solutions of starch. Immediately add, as rapidly as can be done without loss by effervescence, 15 grams of sodium bicarbonate, free from lumps, using a drop of methyl orange to insure the final presence of a decidedly basic solution. Titrate at once with N/20 iodine solution, deferring the addition of starch as long as possible.

Determine the total arsenious acid by either the official method or Davidson's modification, and subtract the percentage found from that indicated by the above titration. This gives total arsenic acid.

The use of chlorine gas may constitute with some operators an objection to this method, but if a good draught hood is available, this objection becomes of small importance. Chlorine is best generated, for this purpose, by dropping pure concentrated hydrochloric acid from a dropping funnel upon pure potassium permanganate contained in a flask, as this yields a fairly constant and easily controlled stream of gas, free from arsenic. The gas need not be washed.

Samples of London purple, analyzed by this method, gave results agreeing well with those obtained by the official methods, and duplicate determinations may be made to agree with each other to within a few hundredths of a per cent. The time consumed in making a determination is materially shortened and the difficulties of manipulation are decidedly decreased. Moreover, students using the method for the first time experience little trouble in obtaining accurate results, and this was never accomplished when any other method was used.

## ANALYSIS OF THE PIGMENT IN A PAINT WHEN IT CONTAINS A COMBUSTIBLE SUBSTANCE.

BY J. E. THOMSEN.

Received August 13, 1906.

THE separation of a pigment from the vehicle is often very difficult, especially in the analysis of a paint skin or a thoroughly oxidized and dried paint. George H. Hurst<sup>1</sup> recommends the use of strong nitric acid for this purpose, but this cannot be used in the case under consideration because some of the combustible substance will be oxidized and lost. The oil, too, is converted into a greasy substance which can be only partly removed and that with great difficulty.

Professor Stillman<sup>2</sup> recommends the use of petroleum ether, but this fails to dissolve completely an oxidized oil, even when applied under pressure in an autoclave.

We have tried several other solvents without success. Alcoholic potash gives a soluble soap but the pigment is affected in many cases. A graphitic carbon pigment analyzed in this way gives too low results and amorphous carbon cannot be separated from the soap by filtration. Decomposing the soap with an acid will not answer because the oxidized fatty acid is as insoluble as the oil.

We finally tried mixing the paint with alcohol and passing dry hydrochloric acid into the mixture, and found this successful.

About ten or twelve times as much of pure ethyl or methyl alcohol should be used as there is of oil in the paint. The process is best carried out in an Erlenmeyer flask and gentle heating aids the solution, which usually requires about half an hour. After the oil is dissolved it can be filtered from the insoluble pigment and the latter washed on a weighed filter with an alcoholic solution of hydrochloric acid. It is then a simple matter to determine the percentage of carbon or of other combustible matter present.

Iron and some other substances are dissolved and can be shaken out with water after the alcoholic filtrate has been mixed with petroleum ether.

If it is desirable to examine the pigment for graphite or amor-

<sup>1</sup> "Painters' Colors, Oils and Varnish," 2nd Ed., p. 48.

<sup>2</sup> "Engineering Chemistry," 3rd Ed., p. 526.

phous carbon, a weighed portion of the residue is powdered for the purpose. With amorphous carbon this is easy but graphite is best powdered by mixing it with sand or some sharp substance. This sand can afterwards be dissolved by hydrofluoric acid.

About 0.5 gram of the finely powdered carbon is mixed in a dry 100 cc. beaker with 10–15 cc. of strong nitric acid (sp. gr. 1.50), the mixture warmed to 60–70° and 3–4 grams of dry potassium chlorate added and the operation repeated till a yellow graphitic oxide is obtained.

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## ANALYSES OF SPANISH PAPRIKA.

By A. G. STILLWELL.

Received August 23, 1906.

THE question of grading these peppers has been giving some trouble to importers, as there have been no standards for various grades, and some peppers entered as low grade, and running up to and over 10 per cent. ash, have been considered as adulterated, when the fact is that they were simply the very lowest grade of goods, being the sweepings from the floors of the mills and containing stems, seeds and dirt which had dried and fallen from the peppers when brought to the factory. This grade of pepper is used as horse and chicken feed and incidentally to bring down a high paprika to medium grade.

The samples were analyzed by methods of the A. O. A. C. They were furnished by a large importer who vouches for them as being true samples of the various grades specified and imported into this country.

The last three analyses are of samples of hot and sweet paprika grown by the U. S. Department of Agriculture and were received by me from the same importer in their original condition, unground.

*Ash.*—It will be noticed that the water-soluble portion of the high-grade peppers is very high, while the part insoluble in acid is very low. As the grade deteriorates, the water-soluble portion is lowered, the acid-soluble and insoluble being correspondingly raised, thus showing the presence of extraneous dirt.

*Ether Extract.*—In regard to the ether extract, the peppers composed of pure shell are very uniform as regards volatile and

Classification.	Total ash.	Soluble in water.	Insoluble in water.	Insoluble in acid.	Ether extract. Volatile.	Ether extract. Non-volatile.	Total extract.	Crude fiber.	
A.A.	7.20	6.40	0.70	0.10	0.95	10.85	11.80	15.75	Shell only, extra quality.
A.	7.20	6.20	0.90	0.10	0.75	11.00	11.75	.....	Shell only, special.
X.	7.75	6.70	1.00	0.05	0.40	8.95	9.35	.....	Fine first.
G.	7.20	6.00	0.95	0.25	0.60	10.05	10.65	.....	Fine second.
S.	6.75	5.05	1.45	0.25	1.15	13.87	15.02	14.75	Semi-shell, first shell, seed little.
F.	6.45	4.25	1.95	0.25	1.00	15.75	16.75	15.50	Semi-shell, second shell and more seed.
G.	6.42	3.12	2.90	0.40	1.10	18.25	19.35	21.00	Regular shell, more seed.
H.	6.40	2.45	3.30	0.65	1.00	19.45	20.45	21.25	Low-grade, poor peppers, and seeds from good peppers.
Y.	6.60	2.45	3.20	0.95	0.72	19.83	20.55	20.90	Low-grade, same plus stems.
B.	7.50	5.40	1.65	0.45	1.10	18.15	19.25	14.40	Shell only, fine but 10 per cent. olive oil added.
D.	6.50	4.85	1.40	0.25	0.80	16.85	17.65	14.50	Semi-shell first plus 10 per cent. olive oil.
J.	6.10	3.95	3.60	0.35	0.30	16.90	17.20	14.35	Second-grade hot pepper.
P.	6.20	4.45	1.40	0.35	2.10	15.20	17.30	10.15	Superior, pure shells, hot pepper.
No. 1	9.30	6.45	1.40	1.45	2.45	8.30	10.75	20.45	Low grade, mercantile, Hungarian.
No. 2	12.45	5.70	4.25	2.55	1.35	6.25	7.60	21.05	Low grade, mercantile.
King.	7.75	4.85	2.00	0.90	0.95	12.35	13.25	.....	Medium grade.
U.S.	4.20	2.80	1.30	0.10	19.70	0.35	20.05	.....	Hot paprika seeds.
U.S.	5.20	4.60	0.60	none	8.75	0.80	9.55	.....	Hot shells.
U.S.	5.50	4.70	0.80	none	8.95	1.05	10.00	.....	Sweet shells.

Nos. 1 and 2 and King are Mercantile Hungarian.  
U. S. are from the U. S. Department of Agriculture.

A.A. to D., inclusive, are sweet Cascara Spanish paprika.  
J. and P. art hot Spanish paprika.

non-volatile extract, but when we come to the peppers containing seeds, the extract immediately *increases* to as high as 20 per cent.

It is the custom to bring up the rich red color of those peppers lacking in color, by adding about 10 per cent. of olive oil (the high-grade peppers are sold almost entirely on color). On this account I should look with strong suspicion on a high-grade pepper containing more than 12 per cent. total ether extract, as is shown by tests of Samples B and D, this to apply only to the sweet peppers as it will be noticed from the Sample P of pure high-grade hot peppers that the extract is 17.30 per cent., though it may be that this sample has had olive oil added. I was unable to get the purity of this sample vouched for.

*Crude Fibre.*—The crude fibre of the peppers containing no stems is fairly uniform at 14 to 15 per cent., while the low grades running up to 20 to 21 per cent. contain stems, seeds, etc.

#### CONCLUSION.

For a pure pepper of high grade (sweet) I would set the standards at: Total ash, 7 to 8 per cent.; water-soluble, 6 to 7 per cent.; water-insoluble and acid-soluble, to 1.25 per cent.; acid-soluble, to 0.30 per cent.; volatile extract, to 1.10 per cent.; non-volatile extract, 8 to 11.50 per cent.; fiber, 15 to 16 per cent.

For second grades containing some seeds: Total ash. 6 to 8 per cent.; water-soluble, 2 to 5.50 per cent.; water-insoluble and acid-soluble, 1.5 to 3.5 per cent.; acid-soluble to 1.00 per cent.; volatile extract, to 1.25 per cent.; non-volatile extract, 13 to 20 per cent.; fiber, 14 to 22 per cent.

For lowest grade, containing practically nothing but seeds and stems: Total ash, 9 to 13 per cent.; water-soluble 5 to 7 per cent.; water-insoluble and acid-soluble, 2 to 4 per cent.; acid-soluble, to 2.5 per cent.; volatile extract, 1 to 3 per cent.; non-volatile extract, 16 to 21 per cent.; fiber, 18 to 22 per cent.

## AN ACCURATE COMMERCIAL METHOD FOR THE ANALYSIS OF SUGAR BEETS.<sup>1</sup>

BY DAVID L. DAVOLL, JR

Received September 6, 1906

THE indirect analysis of the sugar-beet by the juice method and the use of the transposing factor so much in vogue in the United States is open to serious objections, for while it does not affect the price paid by the factory, provided a reasonable control is kept over the factor by frequent direct analyses, it is bound to work injustice to individual farmers, while at the same time unduly favoring others.

It has been our experience that the factor progressively diminishes as the harvesting and the beet-storing season advances, varying from 0.95 in early September to 0.88 in late January.

Frozen beets offer serious obstacles to the indirect method and this condition may occur in most northern states any time after November 1st.

• A factory slicing 1,000 to 1,200 tons of beets per day must be in a position to make in its receiving laboratory from 400 to 500 analyses per day of ten working hours, and with the minimum working force. In good weather 500 ton houses must handle this number.

The practical workings of the much recommended instantaneous aqueous method have not been such as to secure its adoption, and about 125 samples a day is the limit to the number that may be analyzed with any degree of accuracy by one chemist and assistant in one day, using the ordinary method of hot water digestion in a flask. The latter method is outlined as follows:

"Ten cc. to 16 cc. of solution of lead subacetate of 54.3 Brix are placed in a 201.2 cc. sugar flask and 52.096 grams of shredded beet are introduced by means of a glass rod assisted by a spray of water; the volume is finally completed to about 190 cc. A little ether is added to beat down the foam and the whole heated in a water-bath at 80° for thirty minutes, rotating the flask from time to time to promote extraction and facilitate the escape of air bubbles. Water is occasionally added so that the volume is completed to the mark at the end of thirty minutes. Cool to

<sup>1</sup> Read before the Sixth Congress of Applied Chemistry, Rome, Italy, April, 1906.

room temperature, add ether to dissipate any remaining foam, dilute with water to the mark, mix thoroughly and filter."

The criticisms of this method are the following: The introduction of the beet pulp into the flask is painstaking and time-consuming, a medium fineness of a shredded nature giving most trouble. The rotation to secure proper extraction and get rid of occluded air, when properly attended to, requires much attention and the repeated addition of ether, while careless operators, in practice, neglect rotation, particularly when in a hurry. Where 26.048 grams are used in 200.6 cc. dilution, the manipulation is more satisfactory, but the use of 200 mm. tubes requires the objectionable doubling of the reading. A double normal should always be taken in commercial work, being more representative of the original sample, since perfectly intimate mixing cannot be counted upon where the chemist is dependent upon the unscientific helper to prepare the sample. Rapid and uniform cooling cannot be obtained without stirring the flask contents, which is difficult. After adding the final quantity of water, intimate mixing of the water content, which is absolutely essential, is rendered difficult by the presence of the pulp.

The author has overcome the objections to the method of hot water digestion mentioned above by substituting a beaker for the flask, and finally completing the mass to a certain weight, *i. e.*, 209.2 grams, instead of volume. A definite weight of water, and therefore a fixed volume of water also, cannot be added to a normal or multiple thereof of shredded beet, unless it first be ascertained that the diminishing volume of the definite weight of beet, due to increased specific gravity of the constituent juice with rise of sugar percentage, is without influence upon the polarization within the limits of accuracy of the saccharimeter. The Kaiser-Sachs modification of Pellet's instantaneous diffusion directs the weighing of a quantity of water, *i. e.*, 172 grams, where a normal of pulp is used, into the counterpoised flask containing the lead solution. In a modification of this same instantaneous method by cold digestion, Fr. Sachs and A. LeDocte, while measuring 5 cc. solution of lead subacetate and 177 cc. water upon 26.048 grams of shredded beet contained in a copper capsule, in effect use the principle of weighing.

If a strictly representative juice could be expressed from the beet it would be possible to ascertain its specific gravity and thus

calculate the gross weight of pulp, lead subacetate solution and water necessary to complete the volume to 201.2 cc. for beets of different sugar percentages. Obtaining the total solids in the beet and from this subtracting the marc, while giving the real Brix or total solids in the juice, would not give the Brix by "spindling," having its equivalent in specific gravity, for well-known reasons.

Ordinarily the quantity of lead subacetate solution to be used may vary according to the condition of the beet, whether it be fresh and normal or unripe, spoiled, frozen or has been preserved in silos. At the moment of adding the lead subacetate the chemist can scarcely be expected to detect any of these conditions and will be guided considerably by the season, by experimentation with various quantities and noting the effect of lead solution upon the clear filtrate. The first step in the investigation was to ascertain how much would be the weight of 52.096 grams of pulp, 14 cc. of lead subacetate solution and water when mixed, digested, cooled to 20° (the average room temperature) and diluted to exactly 201.2 cc.; or if the weight varied, to establish that variation. Sixty-one individual analyses were made in the following manner: The weights of the clean, dry, 201.2 cc. flasks were carefully ascertained and the capacities in Mohr cubic centimeters determined. This latter was found to vary between 200.76 cc. and 201.2 cc. which, while influencing the weight of the contents and is of importance in the experiment, does not affect the polarization.

The several analyses were then made in the usual manner of the hot water digestion, the flask carefully wiped outside and, with its contents, weighed and the polarization made. The weight of flask contents and the polarization were then corrected to 201.2 cc. capacity at 20°. The weight of the flask contents was found to vary between 207.67 grams (for 11.9 per cent. beets) and 210.08 grams (for 17.9 per cent. beets) with the average of 209.2. This latter may be taken, therefore, as the correct weight to which the mass may be adjusted in water digestion for beets in the receiving laboratory or for *cossettes* at the diffusion battery. It might be remarked here that the beets are purposely selected so as to get as many types as possible, as regards shape, size, degree of ripeness, sugar contents and frozen. The selection rep-



resents the pick of 500 to 600 tons passing along the conveyor to the automatic scale.

Upon the basis of the weights, corrected as above stated, a calculation was made to see how much the polarizations would have been affected had the weight at the end of the analysis been made up to 209.2 grams in every case, *i. e.*, to the average weight and a constant quantity. The differences, partly plus and partly minus, in some instances showed no variation at all, in others inappreciable, and in all cases, with beets containing less than 17 per cent. sugar, they were well within the limits of accuracy of the polariscope.

The average of the minus differences was 0.023 per cent., and of the plus differences 0.03 per cent., with the four extreme results showing 0.09, 0.06, 0.06 and 0.079 per cent. In these four cases, as in forty-eight other analyses, single beets *only* were taken, while in the remaining nine analyses but two beets were united. This was for the purpose of detecting any great irregularities due to individuals, but in a receiving laboratory or cossette analysis, where very many beets are united for one test, any peculiarities would sink into insignificance and show no eccentricities in variation.

The author has, therefore, dispensed with the use of a flask altogether in the analysis of beets and cossettes by the method of hot water digestion during the last sugar-making season, substituting therefor a glass beaker, which is superior to a container of any other material because its weight can be kept constant.

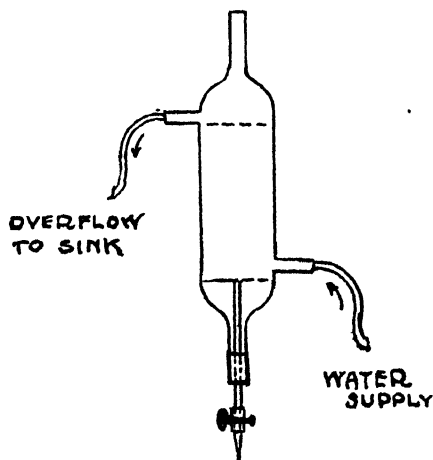
Many thousand individual analyses to determine the purchase price were made with accuracy, speed and cleanliness, and it was well demonstrated that from 600 to 700 analyses may be made by one chemist, one assistant and one wash boy in a day of ten working hours.

The preparation of the digestion beaker was as follows:

A quantity of 300 cc. Jena beakers was purchased, amounting to perhaps 200 in number; they were placed upon a balance, one at a time, and the heaviest selected. This was then provided with a  $\frac{3}{16}$ -inch tube of glass, sealed at both ends, provided with a rubber tip secured by copper wire, of suitable length to act as a stirrer. This heaviest beaker and its stirrer were then carefully weighed, and this weight was taken as the standard weight to which all flasks and their respective stirring rods were to be brought. A

metallic counterpoise was then made. In preparing the stirring rods for the other *lighter* beakers, metallic mercury was introduced into the hollow stirring rods, previous to sealing, in amount sufficient to bring them all up to the standard weight, *i. e.*, the weight of the heaviest and its stirrer, after which they were sealed. The beakers were then etched with consecutive numbers and the stirring rods as well to correspond.

The plan for handling the samples was as follows: After throwing the weighted pulp into the beaker, the weighing dish was rinsed free of traces of pulp into the beaker by means of an overflow pipette. This pipette can be home-made, and is best constructed from a glass condenser-jacket, as shown in the illustration, which practically explains itself. It is always filled



to the same level, but the quantity drawn off is regulated at the lower dotted line by sliding the glass tube up or down. The quantity to be drawn off is first determined by experiment and should be sufficient in amount to allow for evaporation during the half hour digestion at  $80^{\circ}$ . With the large bath in use this is a very uniform amount, and after cooling, the addition of from four to five drops of water completes the mass to 209.2 grams, plus the weight of the beaker and stirrer.

Two baths are necessary, one for digesting and one for cooling, and each should accommodate five baskets of ten beakers each at one time. The baskets are best made of galvanized iron perforated with holes, provided with handles which act as hangers

and having *double* brass wire strung across for keeping the beakers about  $\frac{3}{8}$  of an inch apart. These two wires, side by side, passing between each beaker, prevent clashing and resulting breakage. The bottom is lined with two-ply rubber, perforated.

The farmer's tickets accompanying the sample are placed in a tin case having a large brass number soldered to it, and a corresponding number is upon a basket. The basket, placed with the number facing the chemist, is filled with beakers in a definite order, and the sample tickets are slipped into the corresponding tin box in a similar order or arrangement.

After digestion and cooling, the beaker is wiped outside (or allowed to drain and dry) and placed upon a balance, and with the contents brought with a few drops of water to the desired mass, *i. e.*, 209.2 grams plus the counterpoise. The analysis is then completed as usual.

This method will of course apply to sugar-cane and bagasse analyses, where, weight being applied instead of volume, the quantities may be proportionately increased and the difficulty in sampling thereby overcome.

CARO, MICHIGAN, March 10, 1906.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE].

## THE RAPID DETERMINATION OF WATER IN BUTTER.

BY G E PATRICK

Received August 11, 1906.

SINCE the laws regulating the percentage of water in butter have come into vogue there has grown up a persistent demand for some method whereby the butter-maker, the renovator and the butter merchant can easily and quickly determine the amount of water in his product or his commodity. The most exacting demand is that of the butter-maker in the creamery, or the churn-man in the renovating factory, who needs a method which will yield its results in a few minutes, while his butter-worker stands waiting with its load, further working to be dependent upon the result of the test.

The writer has studied this problem at intervals for two years or more and has at last found a method which is sufficiently accurate, and at the same time so simple in principle and so rapid

in execution that it appears in large measure to meet the demands of the butter-maker.

At the outset of his investigations, before the idea of this simple method had suggested itself, the writer studied first, and very exhaustively, Poda's method<sup>1</sup> which seemed the most promising of the sulphuric acid centrifugal methods proposed up to that time, but to his disappointment found it quite inadequate for the purpose in view, both as regards speed and accuracy. Next he tried several rather elaborate schemes which presented themselves to mind, all attractive in theory but all proving unsuccessful in practice, for which reason it is needless to detail them here.

Finally, discouraged in these more elaborate lines of effort, he turned back to the familiar, commonplace principle of expelling the water by heat; but the ordinary way of doing this, namely, at the temperature of boiling water, is far too slow, requiring several hours' time, so a glycerol bath, easily affording a temperature upwards of 150°, was arranged of form and size to allow of immersing, to the neck, a tall slim flask (assay flask) containing the weighed portion of butter. In this way the water was expelled in twelve to fifteen minutes, the temperature being kept at 150° to 155°, and the whole determination, including both weighings, was completed in about twenty-five minutes.

The results were sufficiently accurate, and the method seemed promising, but the time consumed by the test was still too great, and moreover, the glycerol bath—one of sufficient size to allow of immersing the flask in an inclined position, to prevent loss by spattering—had to be heated up beforehand, and this required quite a long time. How to further shorten the time demanded of the operator was the question.

This change of plan suggested itself: To replace the assay flask by a wide test-tube, to boil off the bulk of the water *over a naked flame*—there being no danger of too high a temperature at this stage—and to finish the drying in a *small* glycerol bath, deep and narrow, in which the tube could at that stage be held vertical without danger of loss by spattering. Such a bath was made of a piece of steam pipe 15 cm. long and of 38 mm. bore, capped at the lower end, and at the upper end screwed into a

<sup>1</sup> Z. Unters. Nahr. Genussm. 4, 492 (1901).

cup-shaped "floor-plate," by which the whole was suspended by a firm ring support. It was charged with only four fluid-ounces (about 120 cc.) of glycerol; a "dummy" tube, kept in the bath while it was heating, raised the surface of the glycerol to the mouth of the bath. The flame of an alcohol<sup>1</sup> lamp heated this bath in fifteen minutes to 130–140°, a temperature high enough to finish the drying of the sample in three to five minutes, after the water had been nearly all expelled by the naked flame.

The plan worked well, but still required about twenty minutes for the complete test; and to regulate the temperature of so small a bath required considerable attention.

All of the above is preliminary, by way of reaching the important point, which is this: After a few trials it was found that just as good results could be obtained by *dispensing with the bath entirely* and drying the sample completely over the naked flame, of course using due care not to overheat. That satisfactory results could be obtained in this manner, uniformly, was a surprise; but the writer has obtained such results on many samples of both creamery and renovated butter, so many in fact that he does not hesitate to declare the method perfectly feasible and that it will give sufficiently accurate results for the purpose here in view, in the hands of any careful person, with a little practice. The complete test, including both weighings and the calculation, can be made in fifteen minutes, and after a little experience the results obtained will seldom if ever be more than 0.3 per cent. from the truth, and frequently less than 0.1 per cent.

The most objectionable feature of the method, from the standpoint of the butter-maker, is that it requires a good balance, one sensitive to say 5 mg. In his own experiments the writer weighs to 1 mg. or less, but this is not necessary. The amount of butter taken for the test may vary from 10 to 18 grams; 12 to 16 grams is perhaps the best amount. With such a charge an error as large as 15 mg. means only 0.1 per cent.

Beside the balance the only things required are:

An alcohol lamp with a wick (made of ball wicking) about 17 mm. thick and giving a flame 75 to 90 mm. tall. It should stand in a place free from drafts in order to afford a steady flame.

Test-tubes—several should be kept on hand to provide for

<sup>1</sup> An alcohol lamp was used in all of this work because gas is not available in most creameries.

breakage—190 mm. in length and 35 mm. inside diameter, made of rather thin glass, of a quality especially adapted to stand boiling.

A small beaker to hold the tube upright while it is being weighed and charged.

A strong wire test-tube holder, large and strong enough to hold the tube firmly while it is shaken and rotated during the heating.

A charging tube—a tube of heavy glass, 140 mm. in length and of 21 or 22 mm. inside diameter—open at both ends, and a ramrod, of any material, fitting loosely into this tube, to force its contents through. In the laboratory a test-tube makes a convenient ramrod.

To charge the tube, small portions of butter, taken with a knife from the homogeneous sample to be tested, are successively forced into one end of the charging tube until it is judged that 12 to 16 grams have been secured, the tube is then lowered, clean end down, well toward the bottom of the previously weighed or counterpoised test-tube, and the butter forced out by the ramrod. Or the butter, in a semi-fluid state, may be poured directly into the test-tube.

The weight being taken, the drying is conducted in the following manner.

The tube, gripped firmly with the tube-holder a little above the charge, is heated at first cautiously, and throughout the operation with almost constant rotation, in order to avoid local overheating—with renovated butter to avoid, also, violent boiling and spattering. The first foam (referring now to genuine butters, for renovated butters produce no foam) can usually be dispersed by merely shaking the tube, but the foam which appears later, after most of the water is boiled off, and which will overflow the tube unless the heating be cautiously done at this stage, is persistent and can be dispersed only by heating the *upper part* of the tube, passing it repeatedly through the flame, lengthwise, exposing first one side and then the other to the heat, and by *vigorous* shaking. This flaming of the tube above the charge is often useful even before the final foaming occurs, as it facilitates the dispersing of the foam later, when it threatens to overflow the tube. During the boiling off of the water the tube should be held inclined at an angle of 45°.

When the large mass of foam has been nearly all dispersed in

the manner described, the lower part of the tube is again heated enough to make certain that no more foam can be produced, but not enough to cause any decided darkening in the color of the butter. The drying is then completed by alternately heating the tube *above the charge*—passing it repeatedly through the flame as before—and rotating vigorously to throw the fat and remaining foam upon the heated glass. The temperature of the latter should be just below that at which it will “sizzle” when touched by the moistened finger. This treatment, continued for a minute or two, will reduce the foam to a layer of not more than 3 to 6 mm. in thickness and will slightly darken the color of the butter. This will now be of a light muddy yellow, or a pale brownish yellow, or perhaps even a dark orange-yellow color, depending upon the original color of the butter, which should be carefully noted at an earlier stage of the operation. More than a moderate discoloration should be avoided, as indicating overheating. The small amount of foam remaining contains only a very minute quantity of water, if indeed any at all. As much of the foam should be dispersed as possible, with only slight discoloration of the butter.

With renovated butters the chief danger to be guarded against is loss by sputtering or violent boiling. Such loss is avoided by cautious heating, by rotating the tube almost constantly, and by holding it inclined even more than  $45^{\circ}$  from the vertical, after the boiling has begun. When the water has been nearly all boiled away, that condensed upon the walls of the tube is expelled by flaming the latter, in the manner described for dispersing the foam of genuine butters. The charge is then heated again cautiously, with *vigorous* rotation of the tube, which is now held vertical, until it is evident that all water has been expelled from the curd covered by the butter oil—this point being determined by frequent examination—care being constantly taken to avoid discoloration of the curd, so far as this is possible. Then the tube, above the charge, is again flamed cautiously, in the manner previously described, to complete the drying. The curd on the sides of the tube should now be no more discolored than to a pale lemon-yellow, while that on the bottom will be considerably darker, ranging from muddy orange-yellow to brownish yellow or yellowish brown. After cooling, the colors are a trifle darker than when the tube is hot. The aim should, of

course, be to discolor the curd as little as possible, while completely drying it.

The tube is now cooled, first with warm or hot water, cautiously at first to avoid breaking, then with cold water at about 15°, until the tube feels cold to the hand, then wiped dry and immediately weighed.

These details take long to describe and the process sounds difficult, but it is not, as a little practice will convince any one. Any careful person can, after a little practice, make the test successfully.

As regards the use of this method by the butter-maker for his immediate guidance in the working of his product, the greatest difficulty lies not in making the test, but in quickly obtaining a small sample for testing that truly represents the large mass of butter in the worker—at least such is the opinion of the writer at the present time. Also, the question presents itself, how nearly does a true sample of the finished butter as it lies in the worker, agree in respect to water content with a true sample of the same butter after it is packed in tubs?

[Definite knowledge upon these points is desirable, and must be had before a rigid interpretation can be placed upon the results obtained with any immediate control-test in the butter factory.

Just as this article is being sent to the Journal the writer learns that a method almost identical with the one here described is in use in certain creameries in the West. The principle is identical. The butter sample is dried in a flask, directly over the flame of a gasoline torch, according to the oral information received.

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[CONTRIBUTION FROM THE DIVISION OF FOODS, BUREAU OF CHEMISTRY,  
U. S. DEPARTMENT OF AGRICULTURE. SENT BY H. W. WILEY]

### DETERMINATION OF SALICYLIC ACID IN CANNED TOMATOES, CATSUPS, ETC.

By W. L. DUBOIS

Received September 6, 1906.

IN THE course of the regular food inspection work of this Bureau we have had frequent occasion from time to time to examine canned tomatoes for salicylic acid. The methods in use for the determination of salicylic acid in this class of goods have been very unsatisfactory, and frequently gave negative results when there



was good reason to believe that the preservative was present. To solve this problem and devise a method which could be successfully applied to canned tomatoes, catsups and similar products the work herein described was undertaken.

As is well-known ether extracts from many foods substances which seriously interfere with the color reaction between salicylic acid and ferric salts. In order to meet this difficulty the food must receive some preliminary treatment which removes these interfering extractives, or the salicylic acid must be taken up from the ether extract by a solvent which will not dissolve the other substances present. The solvent most commonly used for this purpose is petroleum ether. Our experience with it, however, has been very unsatisfactory. When salicylic acid is mixed with the gummy, highly colored bodies which are extracted from many foods by ether, gasoline dissolves it with great difficulty, and we have found it impossible to get even good qualitative tests in some cases when we had added a liberal amount of the preservative. The ether extract from tomatoes contains bodies which completely mask the color test with ferric salt. Gasoline proving useless for separating the salicylic acid from them, we have accordingly confined our attention to devising a way of rejecting these substances before extraction with ether.

In all the methods tried 50 grams of pulped tomatoes were weighed as a sample and the salicylic acid added. This was considered a better test than adding the salicylic acid to a large quantity of tomatoes and weighing a sample therefrom, owing to the possible difficulty in sampling by the latter procedure.

*Method 1.*—Fifty grams of tomatoes were shaken thirty minutes with 150 cc of water made alkaline with sodium hydroxide. The mixture was centrifuged, the supernatant liquid poured through a filter, and an aliquot portion extracted with ether after acidifying. The residue remaining after evaporating the ether contained considerable coloring-matter and other foreign substances. Method abandoned.

*Method 2.*—Fifty grams of tomatoes and 100 cc. of water were acidified with phosphoric acid and distilled with steam till 250 cc. had passed over. The distillate was made alkaline, concentrated to 100 cc., acidified and extracted with ether. No coloring-matter or other foreign substances were present in the ether residue, but neither was salicylic acid in any quantity. No test

was obtained with samples containing up to 100 mg. per kilogram. In one having present 200 mg. per kilogram, 0.5 mg. was found, corresponding to 10 mg. in the kilogram.

For such samples, separation of salicylic acid by distillation with steam is not quantitative. A very large volume of distillate is required to carry over any amount of salicylic acid, and that amount is only a small percentage of the preservative present. The method is not to be recommended where a better procedure is available.

*Method 3.*—Transfer 50 grams of pulped tomatoes to a 200 cc. flask with 50 cc. of water, and make alkaline with milk of lime. Complete to volume, and filter as large an aliquot portion as possible. Usually 150 cc. to 160 cc. of filtrate may be obtained. Acidify with dilute hydrochloric acid and extract with ether four times, using from 75 to 100 cc. of ether at each extraction. Wash the combined ether solution twice with 25 cc. of water, and distil the ether slowly, allowing the last 20 to 25 cc. to evaporate spontaneously. Take up the ether extract in dilute alcohol, make to a definite volume, and match an aliquot portion against a standard solution of salicylic acid, using a few drops of a 2 per cent. solution of ferric alum to produce the color. The results obtained by this method are shown in the table:

Number.	Salicylic acid added. Milligrams	Salicylic acid Found Milligrams.	Recovered. Per cent.
A.....	2.5	0.0	0.0
B.....	5.0	1.82	36.4
C.....	10.0	5.0	50.0
D.....	20.0	12.5	62.4
E.....	25.0	16.92	67.7
F.....	30.0	22.70	75.7

In the ether extract from A crystals appearing to be salicylic acid were present. No test for salicylic acid was obtained. This led to an investigation of the effect of alcohol on the color produced by ferric salts and salicylic acid and the following experiment was carried out.

A solution of 1 mg. of salicylic acid in 50 cc. of water to which were added 3 drops of ferric solution was used as a standard. The solutions matched against this contained 1 mg. of salicylic acid and various quantities of alcohol in 50 cc. as shown in the table below.

Alcohol in 50 cc.	Reading of standard.	Reading of solution examined.	Salicylic acid indicated in solution. Milligrams.	Remarks.
5	20	20	1.0	
10	18	18	1.0	
15	18	18	1.0	Quality of color not same.
20	20	21	0.95	Color of sample decidedly bluer.
25	20	27	0.74	Color quality identical.
30	20	37	0.54	" " "
35	18	...		Color of sample too light to read.
40	18	...		" " " " " "

It appears from these results that the presence of more than a small amount of alcohol in the solution used is inadvisable. We, accordingly, have abandoned its use and are now dissolving the ether extract in warm water, cooling, and making to volume.

It is also an improvement to make the tomatoes alkaline with ammonia before adding the milk of lime. When this is done about 15 cc. milk of lime (200 grams quicklime in 2000 cc. water) are sufficient, whereas much more is necessary when the ammonia is not used. These two modifications in the method given above have solved the problem and give us excellent results as is shown by the following figures:

Salicylic acid used. Milligrams.	Salicylic acid recovered. Milligrams.	Recovered. Per cent.
5	4.7	94.0
10	8.0	80.0
10	8.11	81.1
15	13.33	88.8
20	19.20	96.0
25	25.00	100.0
30	26.70	89.0
50	46.9	93.8

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE. SENT BY H. W. WILEY.]

## A STUDY OF THE METHODS FOR THE DETERMINATION OF ESTERS, ALDEHYDES AND FURFURAL IN WHISKY.

BY L. M. TOLMAN AND T. C. TRESCOT.

Received August 15, 1906.

IN THE course of an examination of a large number of whiskies made in the Bureau of Chemistry under the direction of H. W. Wiley the following work on the methods for the determination

of the ethereal salts, aldehydes and furfural was undertaken, as the methods adopted provisionally by the Association of Official Agricultural Chemists as published in Bulletin 65 of the Bureau of Chemistry were found to be unsatisfactory.

#### DETERMINATION OF ESTERS.

The provisional method as adopted by the Association of Official Agricultural Chemists in 1903 for the determination of esters is as follows:

Neutralize the residue left after distillation in the fusel oil determination with N/10 sulphuric acid and add an excess of 10 cc. of the acid. Allow to stand five minutes, and make up to 200 cc. Titrate two portions of 25 cc. each, using as indicators methyl orange in the first and phenolphthalein in the second. The difference gives the amount of alkali necessary to neutralize the organic acids in 25 cc. of the sample. By subtracting from this figure the number of cubic centimeters of alkali required for the free acids and multiplying the result by 0.0088, the number of grams of ethereal salts (calculated as ethyl acetate) in 25 cc. of the sample is determined.

The distillation of fusel oil is conducted as follows: Add a small quantity of alkali to 200 cc. of the sample under examination, and distil slowly, till about 175 cc. have passed over; allow the distilling flask to cool, add 25 cc. of water, and distil again till the total distillate measures 200 cc. It was found, however, that it was exceedingly difficult to carry out this method satisfactorily and, further, that it was very inaccurate, not in reality giving any true ester value.

The first objection is that the method does not state that sufficient alkali must be added in the distillation to completely neutralize the acids and saponify the esters. If this is not done, there is a loss of unsaponified esters. Some of the whiskies required as much as 10 cc. of normal alkali to 200 cc. to accomplish this result.

The second objection is the difficulty experienced in the double titration with methyl orange and phenolphthalein in the dark colored whiskies, it being practically impossible to get two titrations agreeing within a reasonable limit of accuracy. It was also found that there is a considerable loss of volatile esters, which come over in the first part of the distillate before they are

saponified, even though there be sufficient alkali present, and it was found necessary to boil with a reflux condenser before beginning the distillation. The chief source of error, however, is in the action of the alkali on the caramel and invert sugar present in the whisky.

How much this error may amount to is shown in the following table where caramel prepared from pure cane-sugar was treated in the following manner: A weighed amount of caramel is placed in an Erlenmeyer flask and dissolved in 50 cc. of alcohol (50 per cent. by volume). This is exactly neutralized with N/10 alkali using phenolphthalein as an indicator and then 10 cc. of N/10 alkali are added, the flask connected with a reflux condenser and boiled for one hour, then cooled, and the excess of alkali titrated.

TABLE I.—EFFECT OF ALKALI ON CARAMEL.

Caramel Gram	Amount of N/10 alkali used up cc	Time of boiling Hours
0.050	0.70	1
0.100	1.85	1
0.150	2.70	1
0.200	3.60	1
0.250	3.80	1
0.250	4.60	2

This table shows that with 0.500 gram of caramel per 100 cc., which gives a color about equal to a dark colored whisky, we would have 7.6 cc N/10 alkali used up by the caramel, which would be calculated as esters. This would be as much as the volatile esters in most whiskies. If, however, there was also invert sugar present a still larger error would be introduced as is shown in the following table:

TABLE II.—EFFECT OF INVERT SUGAR ON THE ALKALI.

Invert sugar Gram	Amount of N/10 alkali neutralized cc	Time of boiling Hours.
0.050	1.2	1
0.050	1.5	2
0.100	2.9	1
0.150	3.6	1
0.250	5.85	1
0.250	6.95	3

This table shows that invert sugar uses up the alkali to a greater degree than caramel. If this reaction of alkali with caramel and invert sugar were quantitative, the figure might have some

value, but it is not, so that such a determination can have no value in the presence of these substances.

An illustration of this fact is shown in the following results on some brandies:

TABLE III.—RELATION OF THE SOLIDS AND INVERT SUGAR TO THE FIXED ESTERS.

Solids Per cent.	Invert sugar. Per cent.	Amount of N/10 alkali used by 100 cc. cc	Amount of N/10 alkali used by vol esters in 100 cc. cc	Amount of N/10 alkali used by fixed esters in 100 cc. cc.
1.2658	0.845	40.4	10.0	30.4
1.1348	0.820	47.6	8.8	38.8
1.0640	0.685	36.2	6.4	28.8
0.9726	0.596	32.2	7.2	25.0
0.7774	0.500	26.0	7.6	18.4
0.6840	0.392	26.6	4.8	20.9
0.6070	0.313	25.0	3.0	22.0
0.0306		18.8	12.4	6.4
0.0200		14.2	11.4	2.8
0.0054	trace	9.6	9.6	0.0
0.0052	"	16.4	15.4	1.0
0.0042	"	10.0	7.4	2.6

This table shows that the fixed esters increase with the sugar and are in fact dependent upon its presence. If it were not for this fact the determination of fixed esters might be of some value, as the following table on pure whiskies indicates.

TABLE IV.—DETERMINATION OF FIXED ESTERS IN PURE WHISKIES.

Solids. Per cent.	100 cc. of whisky.	cc. N/10 alkali used by Vol. esters. in 100 cc.	Fixed esters. in 100 cc.
0.3264	27.30	8.0	19.30
0.1976	21.20	9.50	11.70
0.1840	18.6	8.00	10.60
0.1690	15.8	5.2	10.60
0.1620	15.10	7.10	8.00
0.1592	13.4	5.8	7.60
0.1356	19.70	7.70	12.00
0.1164	7.70	2.00	5.70
0.0496	6.60	1.80	4.50

It was evident from this work that the provisional method is unsatisfactory and does not give an ester number. It was therefore necessary to determine the esters in a distillate which was prepared in the following manner: Add 25 cc. of water to 200 cc. of the whisky or spirit to be examined and distil off 200 cc.

into a flask guarded with a mercury valve to prevent loss of alcohol. Measure 50–100 cc. of this distillate into a flask, add a few drops of phenolphthalein and exactly neutralize the free acid with  $N/10$  alkali; add 25–50 cc. of  $N/10$  alkali, stopper the flask and allow to stand at room temperature for eighteen to twenty hours, then connect with a single tube condenser and heat nearly to boiling for one-half hour, cool and titrate the excess of alkali with  $N/10$  acid.

The number of cubic centimeters of  $N/10$  alkali used in the saponification multiplied by the factor 0.0088 gives the amount of esters present as ethyl acetate. There should be a considerable excess of alkali to insure the saponification being complete.

The esters may also be determined by connecting the flask with a reflux condenser, instead of allowing them to stand over night, and boiling for one hour, and if only a few determinations are to be made this will be found to be the most satisfactory procedure, but where a large number of determinations are to be made the first scheme is very satisfactory. It was found by experiment that standing over night with the excess of alkali insured complete saponification of the esters without any danger of loss of the volatile esters.

The question as to whether complete saponification could not be obtained in the cold by standing eighteen to twenty hours at room temperature with the excess of alkali was thoroughly tested in the following manner: Duplicates were measured into flasks and the excess of alkali added and stoppered and allowed to stand over night. In the morning one was titrated and the other was heated for one hour with the tube condenser on the water-bath, cooled and titrated. In 30 cases there was no difference between these titrations and the average on 171 determinations was for the cold titrations 4.1 cc.  $N/10$  alkali for 50 cc. of sample and 4.2 cc.  $N/10$  for 50 cc. of the sample that was heated, which indicates that practically complete saponification takes place at room temperature and that the heating for one hour is not necessary, but in a few cases the titration of the cold saponified sample would be low, showing that complete saponification had not taken place. In our experience, therefore, it is safer to complete the saponification by heating as directed in the method.

The samples that were heated on the water-bath always had

a little more color than the samples which were not heated, indicating a little more resinification of the aldehydes, which may account for the slightly higher results obtained by heating.

In order to check up the method of distillation the esters were determined in some artificial brandies before and after distillation. The results of four determinations on the original showed that 9 cc. of N/10 alkali were needed to saponify the esters in 100 cc. while, according to the average on 20 determinations on the distillate, 8.9 cc. were required for 100 cc., which shows that where the esters present are ethyl acetate, as they were in this sample, all are found in the distillate.

This experiment was repeated on five samples of new colorless whiskies with the same result, showing that the method of distillation is satisfactory and that the esters are distilled over completely although this does not prove that in the old, aged whiskies there are not formed esters which are non-volatile but it is impossible to distinguish them from coloring-matters and resinous materials which are affected by boiling with alkali, as has been shown.

#### ALDEHYDES.

BY L. M. TOLMAN

The method for the determination of aldehydes as provisionally adopted by the Association was found to be entirely unreliable and in fact the reagents as given were not correct, as they reacted with alcohol free from aldehydes. The reason for this was that there was not enough sulphur dioxide in the solution. The amount of sulphur dioxide in the solution greatly affects its sensitiveness and the main point to be determined was how to prepare a solution that would not react with pure alcohol and was still sensitive enough. By experimenting with a number of mixtures it was found that a reagent that contained 5 grams of sulphur dioxide to the liter gave only the slightest tinge of color with the pure alcohol and was sensitive to 0.0001 gram of aldehyde in 50 cc. From this it can be seen that it is very necessary that the amount of sulphur dioxide present should be accurately determined and that the use of a solution of sodium bisulphite of a definite specific gravity is not to be relied on in preparing this reagent. If the sulphite is to be used, its strength in sulphurous acid should be determined by use of a standard solution of iodine. Another objection to the Association method was the

\*



fact that the test is made in a 30 per cent. alcohol solution. The objection to using this strength of alcohol is that when most pure whiskies are diluted to this alcoholic strength they are turbid, and this turbidity greatly interferes with the reading of the amount of aldehydes in the colorimeter. The following are the reagents and method finally adopted for our work.

#### DETERMINATION OF ALDEHYDES.

##### *Reagents.*

(1) *Alcohol Free from Aldehydes.*—This is prepared by first redistilling the ordinary 95 per cent. by volume alcohol over caustic soda or potash and then adding 2 to 3 grams per liter of *m*-phenylenediamine hydrochloride, and digesting at ordinary temperature for several days or with an upright condenser on the steam-bath for several hours and then distilling slowly, rejecting the first 100 cc. and the last 200 cc.

(2) *Sulphite-Fuchsin Solution.*—Take 0.500 gram of pure fuchsin and dissolve in 500 cc. of water, then add 5 grams of sulphur dioxide dissolved in water, make up to a liter and allow to stand until colorless.

This solution should be made up in small quantities, as it retains its strength for only a very few days.

(3) *Standard Acetic Aldehyde Solution.*—Prepared as directed in Vasey.<sup>1</sup>

Aldehyde ammonia is taken as the starting point. Grind this in a mortar with ether and decant the ether, repeating the operation several times, then dry the purified substance in a current of air and finally in a vacuum over sulphuric acid. Dissolve 1.386 grams of this purified aldehyde ammonia in 50 cc. of 95 per cent. by volume alcohol, to this add 22.7 cc. of normal alcoholic sulphuric acid and then make up to 100 cc. and add 0.8 cc. to compensate for the volume of the ammonium sulphate precipitate. Allow this to stand over night and filter. This solution contains 1 gram of acetic aldehyde in 100 cc. and will retain its strength.

The standard found most convenient was 2 cc. of this strong aldehyde solution diluted to 100 cc. with 50 per cent. by volume alcohol. One cc. of this solution is equal to 0.0002 gram of acetic aldehyde. This solution should be made up fresh every day or so as it loses its strength.

<sup>1</sup> "Analysis of Potable Spirits," p. 30.

The method of determining aldehyde is as follows: 5 or 10 cc. of the distillate as prepared for the determination of esters are placed in one of the colorimeter tubes and made up to 50 cc. with aldehyde-free alcohol, strength 50 per cent. by volume, placed in a water-bath kept at  $15^{\circ}$  until it reaches the temperature of the bath. Then 25 cc. of the sulphite-fuchsin solution, which is also at  $15^{\circ}$ , is added; the two solutions are thoroughly mixed and allowed to stand in the bath held at  $15^{\circ}$  for fifteen minutes and then compared in the colorimeter with standard aldehyde solutions.

Standards containing 0.0005, 0.0010 and 0.0015 gram of acetic aldehyde are prepared at the same time and under the same conditions. The standard which matches the sample nearest is used for comparison in the colorimeter. If the color of the sample is stronger than any of the standards, less of the sample must be taken, as colors deeper than that produced by 0.0015 gram of acetic aldehyde cannot be compared with accuracy.

The regulation of the temperature at which the test is made is of the greatest importance, as the accuracy of the method is entirely dependent on the temperature being held constant at about  $15^{\circ}$  during the reaction. If this is not done, the color developed in the blank which should be run with every determination, will be so strong as to interfere with the method. In fact it is impossible to do anything with the method quantitatively without controlling the temperature exactly.

The comparisons in the colorimeter must be made as quickly as possible, as the color rapidly deepens if the room temperature is much above  $15^{\circ}$ . The standard aldehyde solution may be checked against the color glasses of the Lovibond tintometer. In our work, following the exact conditions given above, red No. 5 and blue No. 1.25 combined gave the color developed by 0.0005 gram of acetic aldehyde in 50 cc., looking through 42 mm. depth of solution. This, however, should not be taken as a standard but each analyst should compare his reagents, under the conditions under which he is working with the standard glasses. This will be found to be a valuable check on the solutions.

TABLE V.—CALCULATION OF ALDEHYDES FROM COLORIMETER READINGS.

Sample reading.	0.0005 gram standard. Reading 15. Mg.	0.0005 gram standard. Reading 25. Mg.	0.0010 gram standard. Reading 10. Mg.	0.0010 gram standard. Reading 20. Mg.	0.0015 gram standard. Reading 10. Mg.
10		0.80	1.00	1.50	1.50
11		0.76	0.94	1.40	1.40
12		0.72	0.89	1.30	1.30
13		0.69	0.83	1.25	1.25
14		0.67	0.79	1.20	1.20
15	0.50	0.65	0.76	1.15	1.15
16	0.48	0.62	0.73	1.10	1.10
17	0.465	0.60	0.70	1.08	1.06
18	0.45	0.59	0.685	1.05	1.03
19	0.43	0.575	0.67	1.03	1.00
20	0.415	0.56	0.655	1.00	0.97
21	0.40	0.55	0.64		
22	0.38	0.54	0.62		
23	0.365	0.525	0.61		
24	0.35	0.515	0.59		
25	0.33	0.50	0.58		
26	0.315		0.565		
27	0.30		0.55		
28	0.29		0.535		
29	0.28		0.52		
30	0.27		0.50		
31	0.265		0.49		
32	0.255		0.485		
33	0.245		0.48		
34	0.235		0.47		
35	0.23		0.465		
36	0.22		0.46		
37	0.21		0.455		
38	0.20		0.45		
39	0.195		0.445		
40	0.19		0.44		
41	0.185		0.435		
42	0.18		0.43		
43	0.175		0.425		
44	0.17		0.415		
45	0.165		0.41		
46	0.16		0.405		
47	0.155		0.40		
48	0.15				
49	0.145				
50	0.14				

The amount of color developed by acetic aldehyde under these conditions is not in direct proportion to the percentage of aldehyde

present. A standard containing 0.001 gram develops about three times as much color as a standard 0.0005 gram and about one-half the color of a standard containing 0.0015 gram. This necessitated the preparation of a number of curves from which the table as given above was prepared :

This table is used in the following manner : The colorimeter tube containing the standard solution is placed in the colorimeter at a definite reading, say at 25. The tube containing the sample is now placed in the instrument and compared with the standard by moving it up and down until the colors match, which is at say 19. Now suppose the standard contained 0.0005 gram of aldehyde and was set in the instrument at a reading of 25, then look in the column under the 0.0005 gram reading 25 until you come to the place opposite the reading of the sample and there find the milligrams of aldehyde which, in this case, is 0.575. The colorimeter used in this work was that described by Schreiner<sup>1</sup> and it was found to be very satisfactory and convenient, being preferred in this work to the Soleil-Dubosq instrument, as it gives a much wider range of comparison. Schidrowitz<sup>2</sup> does not use the distillate for this determination but clarifies the whisky with basic lead acetate, colors his standard slightly with tincture of galls to match the color of the decolorized whisky, and then treats with the reagent, but this method, while it is applicable to pure whiskies light in color, cannot be applied to whiskies that are colored with caramel, as caramel is not removed by lead acetate. Hence, in order to obtain comparable results, it is necessary to work on the distillates in all whiskies.

The claim that aldehydes are formed in the distillation is not substantiated by our experiments on 150 samples of new brandies in which the determination of aldehydes was made on the original sample and on the distillate. The average on the original was 172 mg. per liter while the average on the distillate was 173 mg. per liter. These results show several things. First, that the method gives comparable results and results that can be duplicated, as in this work the determination on the original was made on one day and the determination on the distillate the next day. Second, that there is no loss or gain in aldehydes by distillation.

<sup>1</sup> This Journal, 27, 1192-1203 (1905).

<sup>2</sup> J. Chem. Ind. 21, 814-819 (1902).

Third, that it is an exact method as is shown by the close agreement of results.

### FURFURAL.

BY L. M. TOLMAN.

Schidrowitz does not use the distillate for this determination but follows the same procedure in the determination of furfural as in the determination of aldehydes. The same objection holds in this method, however, as in the aldehyde determination, namely, that the method cannot be applied to all the whiskies on account of the impossibility of removing caramel when present, so that it is better to use the distillate in all cases.

The following are the reagents and the method used for the determination of furfural: Colorless aniline, hydrochloric acid (sp. gr. 1.125), alcohol free from furfural. The aniline was obtained by redistilling the ordinary dark colored aniline. This must be kept in the dark or it will soon become colored. The ordinary 95 per cent. by volume alcohol redistilled over caustic soda or alkali is practically free from furfural.

*Standard Furfural Solution.*—Prepare the standard furfural solution by weighing 1 gram of redistilled furfural and dissolving it in 100 cc. of 95 per cent. by volume alcohol. This strong solution will keep. Standards for use are made by diluting 1 cc. of this solution to 100 cc. with 50 per cent. by volume alcohol. One cc. of this solution contains 0.0001 gram of furfural.

The method for determining furfural is as follows: 10 or 15 cc. of the distillate as prepared for the determination of esters is placed in a colorimeter tube and diluted to 50 cc. with 50 per cent. by volume alcohol free from furfural. The tube is placed in a water-bath kept at 15° and allowed to remain until it reaches the temperature of the bath. Then 2 cc. of the aniline and 0.5 cc. of the hydrochloric acid are added and the whole thoroughly mixed. The tubes are left for fifteen minutes in the bath at 15°, and then taken out and read in the colorimeter against standard furfural solutions.

Standards containing 0.0001, 0.0002 and 0.0003 gram of furfural are prepared and treated in the same manner. The standard which matches nearest the color in the sample is used for comparison in the colorimeter.

The amount of color developed by the furfural solutions is in

direct proportion to the amount of furfural present, so that calculations can be made directly from the readings.

The temperature greatly affects the reaction and it should be carefully regulated.

Hydrochloric acid was used instead of acetic acid on account of the fact that the acetic acid available gave a very decided color reaction, which interfered with the test. Another advantage of hydrochloric acid is that it is more uniform in quality than acetic acid and in these color tests it is necessary that the conditions shall remain constant in order to obtain comparable results. The occurrence of furfural in acetic acid or some substance that gives a similar color reaction with this reagent seems to be quite common, as it has been noted by a number of observers. The substance that gives the test can be destroyed by heating the mixed reagent, but this interferes with its sensitiveness.

In order to settle the question whether all the furfural will be found in the distillate and also whether there is any formation of furfural in distillation, the determination was made on a number of samples of slightly colored and colorless spirits, in the original and in the distillate.

The results on 120 samples gave an average of 23.4 mg. per liter on the original and of 23.2 mg. per liter on the distillate. This shows that there is no loss or gain of furfural by distillation; it also shows that the method is reliable, as the same conditions held in these determinations as in the work on aldehydes.

## MOISTURE IN COAL.<sup>1</sup>

BY E. E. SOMERMEIER

Received September 17, 1906.

THE determination of moisture in a sample of coal is apparently simple and a result is easily obtained. The proper relation that this result bears to the original sample is, however, not so easily determined. Variations in this relation directly affect the application of all analytical work done upon the sample and the possibility of unaccounted-for moisture losses during the taking, shipping and preparing of the sample for chemical analysis too often receives little or no attention.

The method of determining moisture recommended by the

<sup>1</sup> Published by permission of the Director of the U. S. Geological Survey.

Committee on Coal Analysis appointed by the American Chemical Society<sup>1</sup> is as follows: "Dry 1 gram of the coal in an open porcelain or platinum crucible at 104-107° for one hour, best in a double-walled bath containing pure toluene, cool in a desiccator and weigh covered." The report of the committee also states that "with coals high in moisture and in all cases where accuracy is desired determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter."

The results in moisture obtained by following these directions do not, as is well-known, represent the total but only the loosely held moisture present and it represents this only approximately, as the loss in weight represents not the amount of moisture expelled but the moisture expelled plus or minus any changes due to oxidation, or any changes in weight due to the expulsion of gases from the coal. In most coals the oxidation changes are small and the loss in weight can be considered as representing moisture loss without appreciable error. The process does require, however, close attention to certain details, if uniform and accurate results are to be obtained and the precautions given by the committee to prevent moisture loss in the sample are too often neglected. The experience of the writer is that these precautions cannot be too strongly emphasized.

The precautions and details which experience has shown require careful attention may be considered under the following heads:

(1) It is absolutely necessary that the greatest of care be exercised to prevent moisture changes in the coarse sample while being taken and during transit to the laboratory.

(2) The fine sample for chemical analysis should be in nearly an air-dry condition so as to lessen danger from large moisture changes while in the laboratory.

(3) The air of the oven in which the sample is heated to drive out the moisture should be of a uniformly dry condition, if uniformity in results is to be obtained.

(4) The sample after removal from the oven should be cooled in a desiccator over sulphuric acid.

<sup>1</sup> This Journal, 21, 1119.

*Care in Preparation and Shipment of Sample.*—As a rule precautions to prevent moisture losses during the taking of the sample are not given sufficient attention and the too common practice of shipping the coarse sample by mail or express in canvas bags cannot be too strongly condemned where the moisture result is expected to represent the moisture in the coal as sampled. A sample of coal in a canvas or muslin sack may and usually does lose a large portion of its loosely held moisture while in transit in warm mail or express cars, and the moisture results on such a sample can be only the moisture present in that particular sample in a more or less nearly air-dry condition. This is a point which has been too much overlooked in the past and as a consequence many hundreds of published analyses of coal supposedly representative of the coal as mined really lack as much as several per cent. of the moisture actually present in the sample as mined or shipped.

Failure to guard against moisture losses is not necessarily of serious consequence on samples which have been selected more or less at random and sent to the chemical laboratory for analysis. On such samples the sender understands that the particular results obtained can represent the seam of coal only in a general way. The moisture result on these samples, while low and to that extent misleading, is a minor determination, as the ash and sulphur are usually the determinations particularly desired. When samples from actual steaming tests are handled in this way the unaccounted-for moisture losses will, of course, directly affect the accuracy of the test and the heat balance in such a case is necessarily misleading, as the coal usually analyzes better than the coal as actually fired under the boilers. This makes the unaccounted-for losses larger by perhaps several per cent. than they should be and some coals with an originally high moisture content and consequent high moisture loss may be made to appear superior to really better coals with an originally low moisture content and a consequent lower moisture loss in transit to the laboratory. If correct moisture results are desired, the only safe way is to have the sample shipped from the mine or testing plant in air-tight cans, as was recommended by the committee.<sup>1</sup>

*Handling of Sample in the Laboratory.*—The experience of the writer while connected with Professor N. W. Lord as coal analyst

<sup>1</sup> Loc. cit. p. 1117.



for the Ohio Geological Survey, and especially since his connection with the U. S. Geological Survey Coal Testing Laboratory, is that the only satisfactory method of handling all kinds of coal samples is to subject all or a portion of the coarse sample (5 to 10 pounds in weight) to a rather thorough air-drying before pulverization, weighing the sample from time to time until the loss becomes small. This air-dried sample is then ground in a closed ball mill and when pulverized the portion for analysis is at once put into bottles and securely stoppered.<sup>1</sup>

The drying of the coarse sample to a nearly constant weight by simple exposure to the atmosphere of the sampling room is a slow process, often requiring several days or a week. When a large number of samples are to be handled or where there is any hurry for results the air-drying by simple exposure to the air is too slow and too troublesome. In the U. S. Coal Testing Laboratory to facilitate this drying the samples are spread upon large trays and put into a large drying-oven designed for the purpose. The air of this oven is kept 10° to 20° warmer than the air of the sampling room and is continually renewed by means of an electric fan attached to the upper portion of the oven. By this method the material is usually dry enough to sample in from six to eight hours and can be sampled the day after being received or in special cases on the same day.

The sample as it comes from the oven after the treatment above outlined is described as "air-dried" and the analysis of the laboratory sample prepared from it is designated as the analysis of the air-dried sample. Experience in the laboratory has shown that the percentage of moisture remaining in the coal in this condition is affected to a considerable extent by the temperature and humidity of the air, the nature of the coal, the weight and coarseness of the sample, as well as its age and previous treatment. For this reason, it is not to be considered as a determination of any definitely fixed quality of the coal and it was originally adopted merely as a stage in the sampling in order to make it possible to further handle and pulverize the coal to the condition required for analysis in the laboratory without incurring more than trifling alterations in moisture. Experience has shown, however, that where the method is conducted systematically and

<sup>1</sup> See Preliminary Report of the operations of the Fuel Testing Plant of the U. S. Geological Survey, 1905, Bulletin No. 290.

the drying continued, as is the case at the Testing Laboratory, until the loss between two successive weighings<sup>1</sup> made at least two hours apart is less than 1 per cent. of the weight of the sample, the air-drying loss with rare exceptions lies within a sufficiently definite range to give it some importance as showing the effect of standing and exposure on the percentage of moisture in the coal. This is a matter of considerable commercial importance, as so far as the moisture content is concerned coals having a large air-drying loss are obviously much more affected than coals having a small air-drying loss. It further has appeared that the amount of residual moisture in the air-dried sample prepared under the described conditions usually lies within a range which is somewhat characteristic of different kinds of coal, as from 12-16 per cent. for lignites, 3 to 6 per cent. for Illinois coals and in the neighborhood of 1 per cent. for many of the West Virginia coals.

Understood in this way, the air-drying loss has been deemed of sufficient importance to be worthy of publication in connection with the analytical results. The amount of air-drying loss has also a special significance in the case of wet samples, and the high results for moisture upon samples of washed coal or wet slack are more easily explained and understood when accompanied either by the analysis of the air-dried coal or by the amount of air-drying loss on the coarse sample.

**Moisture Determinations in the Fine and Coarse Sample.**—Our experience is that the preliminary air-drying of the coarse sample and the subsequent determination of the moisture in the fine air-dried sample taken together give much more satisfactory and uniform results than determinations made upon independent coffee-mill samples ( $1/8$ - $1/10$  inches in size) of the undried coal, as while in most coals the results are comparable, with some coals more or less lignitic in character the moisture determinations made on the coarse samples require several hours' heating before giving anywhere near constant weight, as much as several per cent., which will be given off by continuing the heating for one or two hours longer, often remaining in the sample at the end of an hour's heating.

**Moisture in Air of Oven.**—The loss of weight of the sample by

<sup>1</sup> Where the sample is dried by simply exposing it to the air of the laboratory, the time between weighings is at least eight, and, more often, from sixteen to twenty-four hours.

heating for one hour at  $105^{\circ}$  in an ordinary drying-oven represents the moisture in the coal when the sample is dried in laboratory air heated to that temperature. On different days the humidity of the laboratory air varies greatly with the result that the moisture results fluctuate correspondingly, being higher in dry weather when the humidity is low and lower in damp weather when the humidity is high. These variations may be as great as 0.4 or 0.5 per cent. In the U. S. Coal Testing Laboratory to eliminate this error use is made of a special moisture oven designed by Professor N. W. Lord. The oven is constructed with double walls and the space between the walls partially filled with a solution of calcium chloride of such strength that the boiling-point of the solution is high enough to raise the temperature of the oven to  $105^{\circ}$ . Concentration of the solution is prevented by means of a reflux condenser fitted into the top of the oven. Air is admitted into the drying-chamber through a coil of block-tin tubing which passes through the calcium chloride solution. The inner end of the tubing is soldered into the rear wall of the drying-chamber and the outer end is connected to a flask containing concentrated sulphuric acid. During a determination air under pressure is bubbled through this sulphuric acid, passes through the block-tin coil into the drying-chamber and escapes through a small orifice in the door of the oven. The air is passed through at such a rate that a volume equal to the capacity of the oven passes through every six or eight minutes. Most of the moisture of the sample is driven off during the first fifteen or twenty minutes so that by the end of the hour the air of the oven is practically air-dried over sulphuric acid. By working in this way variations in the humidity of the laboratory air do not affect the determinations and duplicates run at different times agree much more closely than where an ordinary air oven is used.

*Use of Concentrated Sulphuric Acid in Desiccators.*—Formerly dry calcium chloride was used in the desiccators in which the samples were allowed to cool after being taken from the oven. From the results of a number of tests it is shown that coal dried at  $105^{\circ}$  has a much greater affinity for moisture than ordinary calcium chloride and the samples, if left in the desiccators for any length of time, always gave low moisture results. Tests with concentrated sulphuric acid as the drying agent in the desiccator show that the sample can remain in the desiccator for several

hours before weighing without affecting the moisture result. On this account all moisture determinations are now cooled in desiccators over concentrated sulphuric acid.

*Chemical Records.*—The air-drying of the coarse sample and the analytical determinations on the air-dried sample necessitate the recalculating of results to obtain the analyses of the "sample as received." The regular analytical records of a sample as kept in the chemical laboratory at the Coal Testing Plant are shown by the following record of the results obtained on a sample of West Virginia coal:

Laboratory sample number .....	1561
	Per cent.
Loss of moisture in air-drying of coarse sample.....	3.10

#### Analysis of air-dried sample :

##### Proximate :

Moisture.....	1.01
Volatile matter.....	29.53
Fixed carbon .....	62.67
Ash.....	6.79
	<hr/>
	100.00

##### Ultimate :

Hydrogen.....	5.04
Carbon .....	79.35
Nitrogen.....	1.63
Oxygen.....	6.39
Sulphur .....	0.80
Ash.....	6.79
	<hr/>
	100.00

	Calories.	B. T. U.
Calorific value determined.....	7984	14371
Calorific value calculated from ultimate analysis .....	7890	14202

The analysis of this sample as received is obtained from the results on the air-dried sample by multiplying each result by  $\frac{100 - 3.10}{100}$  and adding to the moisture result so obtained the 3.10 per cent. loss on the coarse sample and to the hydrogen and oxygen results so obtained this 3.10 per cent. moisture loss in the proportion in which the two elements unite to form water or  $\frac{1}{9}$  of the moisture loss to the hydrogen and  $\frac{8}{9}$  of the loss to the oxygen.

Performing these operations the analysis on the sample as received is as follows:

Proximate:

Moisture.....	4.08
Volatile matter.....	28.61
Fixed carbon.....	60.73
Ash.....	6.58
	<hr/>
	100.00

Ultimate:

Hydrogen.....	5.23
Carbon.....	76.89
Nitrogen.....	1.58
Oxygen.....	8.95
Sulphur.....	0.77
Ash.....	6.58
	<hr/>
	100.00

Calorific value determined—Calories..... 7736

B. T. U..... 13925

The result on the air-dried sample must not be confounded with the "dry coal" of the mechanical engineer, which may be obtained from either of the above ultimate analyses by subtracting from the hydrogen and oxygen shown in the analysis the amount of hydrogen and oxygen present in the moisture of the proximate analysis corresponding to the ultimate, then dividing each of these remainders and each of the other percentages of the ultimate analysis by 100 minus the moisture present in the proximate analysis.

Performing these operations the ultimate analysis for the "dry coal" on this sample is as follows:

Hydrogen.....	4.98
Carbon.....	80.15
Nitrogen.....	1.65
Oxygen.....	5.55
Sulphur.....	0.81
Ash.....	6.86
	<hr/>
	100.00

This seems to be a multiplication of results but all appear to be necessary. The "as received" results certainly cannot be dispensed with, as they represent the actual sample. The results on the air-dried sample are the actual results obtained in the laboratory and are of interest as showing the analysis of the coal

when in an approximately air-dried condition. The chemist has no use for the "dry coal" results but it is necessary to the mechanical engineer in calculating the heat balance by the code prescribed by the American Society of Mechanical Engineers. In the results given under the work of the chemical laboratory in the final report of the operations of the Coal Testing Plant at the World's Fair, St. Louis, Mo., these analyses are all plainly marked "analysis of air-dried sample" and "sample as received." The analyses published in the same report under the report of the Boiler Test Division also have the ultimate analyses plainly designated as "dry coal." In the preliminary report of the Testing Plant for 1905 the different analyses are not so specifically designated but the same general arrangement holds and in all chemical reports any analysis unless otherwise marked refers to the "sample as received." On the other hand, the mechanical engineer using the code adopted by the American Society of Mechanical Engineers uses only ultimate analyses calculated to a "dry coal" basis.

The above explanation of the different methods of reporting chemical analyses may appear unnecessary but may possibly be of use to the many engineers who are not chemists and to the many chemists who are not engineers, and especially to the many who are neither chemists nor engineers but who are interested in coal analysis.

Further data relating to the experiments mentioned in this paper and a more complete description of the apparatus and methods used in the U. S. Coal Testing Laboratory will appear in the final report of the Coal Testing Plant for the year ending July, 1906, which report is now in course of preparation. This report will not, however, be available for some months and the importance of the moisture determinations appears to warrant calling attention to and emphasizing at this time some of the precautions necessary to be observed in order to secure accuracy of results.

CHEMICAL LABORATORY,  
U. S. COAL TESTING PLANT,  
ST. LOUIS, MO.

# THE REMOVAL OF "BLACK ALKALI" BY LEACHING.<sup>1</sup>

BY F. K. CAMERON AND H. E. PATTEN.

Received August 24, 1906.

THE reclamation of soils containing "black alkali," or soluble carbonates, presents unusual difficulties. These difficulties are due in large part to the fact that soils generally show decidedly higher absorptive powers toward bases present in alkaline solutions than when the solutions are neutral or acid;<sup>2</sup> and that the presence of hydroxides or carbonates of the alkali metals frequently induces a "puddling" of the soil, preventing a thorough penetration by water and subsequent removal of the water with its dissolved contents by drainage. Consequently, a laboratory investigation was deemed advisable of two soils which contain "black alkali" and which are now in process of reclamation. One, a sample from North Yakima, Washington,<sup>3</sup> was from the surface eight inches of the experimental tract north of Wide Hollow Creek. The second sample,<sup>4</sup> from the Toft-Hansen tract at Fresno, California, was from the surface eight inches of a spot plainly showing "black alkali" at the surface. When collected there were a few scattering spears of grain on this spot, although all about it the grain had made a good stand. When the crust formed by the "alkali" was broken grain was found which had sprouted but had not been able to push through the crust. A calcium carbonate hard pan was found about three feet below the surface, but was also found at the same depth in adjoining fields on which there was a good stand of barley.

TABLE I.—WATER-SOLUBLE CONSTITUENTS IN SOILS FROM NORTH YAKIMA AND FRESNO, EXTRACTED BY DIGESTING ONE PART OF SOIL WITH FIVE PARTS OF WATER.

	North Yakima. Per cent.	Fresno. Per cent.
Ca .....	trace	trace
Mg.....	0.02	trace
Na .....	0.24	0.13
K.....	0.03	0.02
SO <sub>4</sub> .....	0.18	0.09
Cl .....	0.03	0.03
HCO <sub>3</sub> .....	0.27	0.16
CO <sub>3</sub> .....	0.10	0.02
Total.....	0.87	0.45

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> See Bulletins Nos. 30 and 32, Bureau of Soils, U. S. Dept. Agric.

<sup>3</sup> Sample No. 14,413, Bureau of Soils collection; Soil Survey.

<sup>4</sup> Sample No. 14,402, Bureau of Soils collection; Soil Survey.

Chemical analyses of the water-soluble salts in these samples by the conventional method<sup>1</sup> of digesting the sample with five times its weight of water gave the foregoing results.

It will be observed that both samples were of the same type of alkali soils, containing beside the soluble carbonates, notable quantities of sodium sulphate, with much lesser amounts of other sulphates and chlorides.

From the mechanical analyses of these samples together with their field properties, both the Yakima and Fresno soils would be classified as fine sandy loams.

TABLE II.—MECHANICAL ANALYSES OF SOILS FROM NORTH YAKIMA, WASHINGTON, AND FRESNO, CALIFORNIA.

Diameter. mm	Conventional name.	North Yakima. Per cent.	Fresno Per cent.
2-1	Fine gravel.....	trace	0.1
1-0.5	Coarse sand.....	1.3	2.1
0.5-0.25	Medium sand.....	2.5	3.7
0.25-0.1	Fine sand .....	12.8	24.7
0.1-0.05	Very fine sand ...	21.2	33.6
0.05-0.005	Silt.....	48.6	29.5
0.005-0	Clay .....	13.5	6.2

*Experimental Methods.*—The method of percolation was essentially the same as described by Schreiner and Failyer in Bulletin No. 32 of this Bureau (1906), "The Absorption of Phosphates and Potassium by Soils,"<sup>2</sup> with the exception that a constant water pressure was used instead of attempting to maintain the rate of percolation constant. One hundred grams of soil were placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, and distilled water allowed to percolate through the soil under a constant water pressure of 199 cm., or 6.5 feet.

The volume of each percolate was measured, its electrical conductivity taken with a field bridge, and its time of flow recorded. Normal carbonates ( $\text{CO}_3$ ) and bicarbonates ( $\text{HCO}_3$ ) were then determined volumetrically with standard acid potassium sulphate solution, and the chlorine titrated with tenth-normal silver nitrate solution, using potassium chromate as indicator. Sulphates were not determined because the amounts here involved are too small to have any great agricultural significance, and the analytical

<sup>1</sup> Bull. No. 18, p. 65, Bureau of Soils, U. S. Dept. Agric. (1901).

<sup>2</sup> See also J. Physic. Chem. 10, 239, 361 (1906).



difficulties in handling quantities of this magnitude would be unjustifiably great.

*Results with Soils from North Yakima.*—The data obtained with the Yakima soil are given in Table III. The first column gives the time during which percolation has been progressing; the second column the volume of percolate which has passed; the third column the conductivity of the successive percolates, at 25°, expressed in reciprocal ohms multiplied by 1000, which may be converted to "specific conductivity" by multiplying by the cell factor, 3.57. The next three columns give concentrations in the successive leachings and the last three columns show the total amounts of the several constituents removed from the soil.

An inspection of the results presented in this table (III) shows that while the water which was passed through the soil was kept under a constant head, the rate of percolation was not constant but varied somewhat from time to time. The first water entering the dry soil ran through quite rapidly, but as soon as the soil became saturated, it moved much more slowly. Subsequent variations in the rate of percolation were observed, undoubtedly due in some cases, to "channeling" in the soil, in some cases probably to "silting up" of channels, and in part to the fact that as the percolation proceeded with a consequent decrease in the amount of alkali present, the strongly deflocculating action of this material became less and less, so that the soil behaved as though it underwent a change in texture as well as in structure. For these reasons the concentrations of the successive portions of the percolates, as evidenced by the conductivity as well as the analyses, did not show a *regularly* progressive change, although on the whole, the concentrations became lower and lower as percolation proceeded. These results are in harmony with many field observations where it has been found that the concentration of a drainage water may vary over quite a wide range, depending upon the rate at which the applied water moves through the soil, and upon whether a sufficient length of time had elapsed for equilibrium to result between the salts dissolved and the salts remaining in the soil.<sup>1</sup>

In the present case, chlorides had practically disappeared after 778 hours, when 829 cc. of water had passed through the soil.

<sup>1</sup> See Bull. No. 33, p. 10, Bureau of Soils, U. S. Dept. Agric. (1906); and this Journal, 28, 1229 (1906).

TABLE III.—EXPERIMENTAL DATA FROM NORTH YAKIMA SOIL.

Time in hours.	Volume of percolate passed.	Conductivity of successive portions of percolate $\times 10^3$ , $t = 25^\circ\text{C}$ .	Concentration of successive portions of percolate in parts per million of solution.			Total grams constituents leached from 100 grams of soils.		
			CO <sub>2</sub> .	HCO <sub>3</sub> .	Cl.	CO <sub>2</sub> .	HCO <sub>3</sub> .	Cl.
48	37	.....	84	1,160	193	0.00304	0.0424	0.00715
120	101	.....	196	1,586	110	0.0156	0.1439	0.01420
216	170	5.76	171	753	152	0.0274	0.1962	0.0247
264	242	3.62	223	406	4	0.0433	0.2252	0.02498
312	312	4.07	168	445	2	0.0550	0.2563	0.02512
360	383	3.98	128	403	3	0.0641	0.2849	0.02533
432	473	3.38	89	385	4	0.0722	0.3199	0.02569
480	539	2.94	64	388	4	0.0764	0.3451	0.02595
558	629	2.80	73	321	1	0.0829	0.3740	0.02606
726	739	2.49	73	263	0.7	0.0909	0.4029	0.02615
778	829	2.17	73	218	trace	0.0974	0.4225	
827	917	2.04	67	221		0.1034	0.4420	
873	992	1.90	78	158		0.1093	0.4538	
940	1,097	1.71	78	130		0.1173	0.4675	
988	1,184	1.77	50	170		0.1219	0.4823	
1,065	1,314	1.63	42	185		0.1273	0.5065	
1,114	1,398	1.51	34	164		0.1301	0.5203	
1,163	1,485	1.33	22	170		0.1322	0.5352	
1,210	1,562	1.24	27	145		0.1343	0.5470	
1,259	1,642	1.03	22	127		0.1361	0.5583	
1,306	1,716	1.03	6	139		0.1365	0.5683	
1,378	1,831	1.00	8	130		0.1372	0.5733	
1,443	1,951	0.91	11	109		0.1385	0.5864	
1,499	2,050	0.93	11	115		0.1396	0.5978	
1,566	2,138	0.83	8	103		0.1404	0.6069	
1,614	2,216	0.74	6	94			0.6142	
1,665	2,306	0.71	6	85			0.6214	
1,711	2,378	0.68	6	79			0.6271	
1,785	2,490	0.61	6	73			0.6353	
1,836	2,586	0.59	0	79			0.6429	
1,884	2,673	0.59	0	67			0.6487	
1,932	2,768	0.51	0	67			0.6551	
2,004	2,908	0.45	0	67			0.6645	
2,076	3,028	0.48	0	61			0.6718	
2,148	3,148	0.43	0	55			0.6784	
2,340	3,378	.....	0	51			0.6900	
2,460	3,583	.....	0	47			0.6996	
2,580	3,813	0.51		42			0.7093	
2,772	4,088			42			0.7209	
2,887	4,276			39			0.7283	

Normal carbonates failed to appear in the percolate after 1,614 hours when 2216 cc. of solution had passed. This does not mean, however, that no normal carbonates remained in the soil for, as has been previously shown in this laboratory,<sup>1</sup> dilution of a normal carbonate causes a change with formation of more bicarbonate. It is certain that the amount of normal carbonates in the solution has been reduced to a point below that dangerous to plant growth. The alkali in the form of bicarbonates, however, continued to be leached from the soil after percolation had proceeded for 120 days and a total volume of over 4200 cc. had passed through the soil. The results are readily seen in Fig. 1, where the abscissas

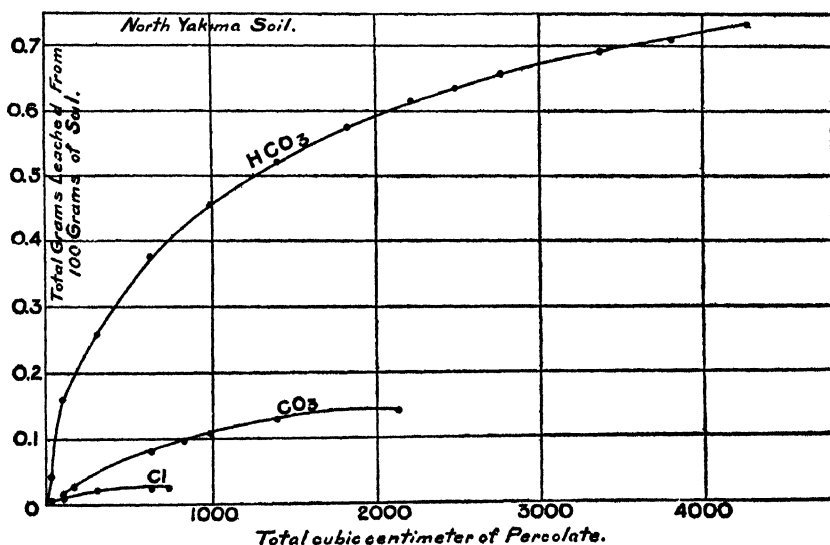


Fig. 1.

are total volume of percolate and the ordinates, total grams of the several constituents removed from the soil. It will be observed that the curves are asymptotic. In the case of the chlorides and normal carbonates, as noted above, the amounts in the successive portions of percolate soon become too small to determine accurately, but in the case of the bicarbonate amounts could still be readily determined, while the run of the figures in the table and the shape of the curve show that at the time the experiment was terminated the amount in the successive portions

<sup>1</sup> Cameron and Briggs: Bull. No. 18, p. 14, Bureau of Soils, U. S. Dept. Agric. (1901); J. Physic. Chem. 5, 537 (1901).

of percolate was diminishing so slowly as to be almost constant. This is brought out more clearly in Fig. 2, in which the ordinates

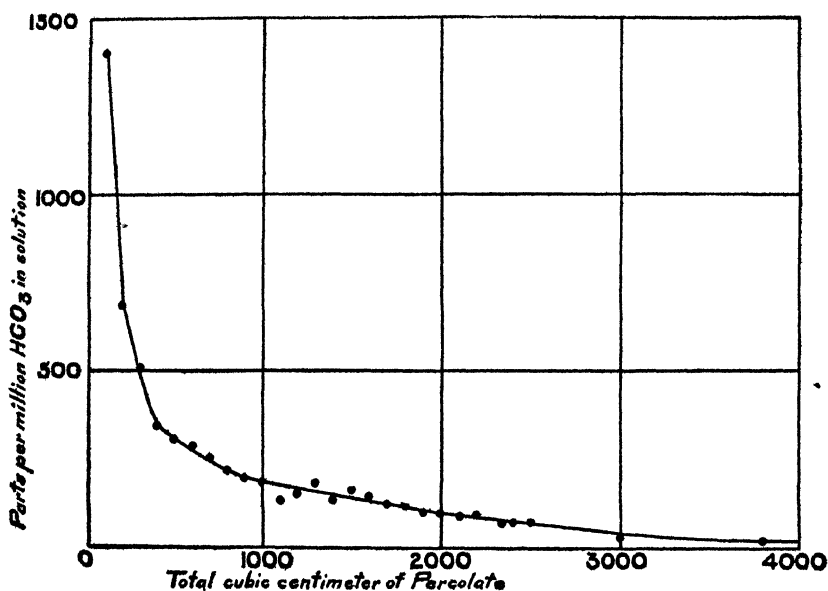


Fig. 2

represent the concentrations in parts per million in successive portions of the percolate. The results in this chart are calculated from the curve in Fig. 1, rather than from the actually observed values, in order to avoid the accidental experimental errors noted above, and thus obtain a more accurate idea of the nature of the curve. This result is analogous to former leaching experiments made in this laboratory. An inspection of the results for bicarbonates shows, moreover, that, if the first few observations be disregarded, the leaching curve is described with fair accuracy by the equation

$$\frac{dy}{dv} = K(A - y),$$

proposed by Schreiner and Failyer.<sup>1</sup>

*Results with Soils from Fresno.*—In working with the Fresno sample the same experimental difficulties were encountered as with the Yakima sample, in that changes in flocculation and channeling materially affected the rate of leaching. In Table IV

<sup>1</sup> Bull. No. 32, p. 23, Bureau of Soils, U. S. Dept. Agric. (1906).

are given the rates of leaching during the earlier part of the experiment. The results are more clearly shown in Fig. 3. It will

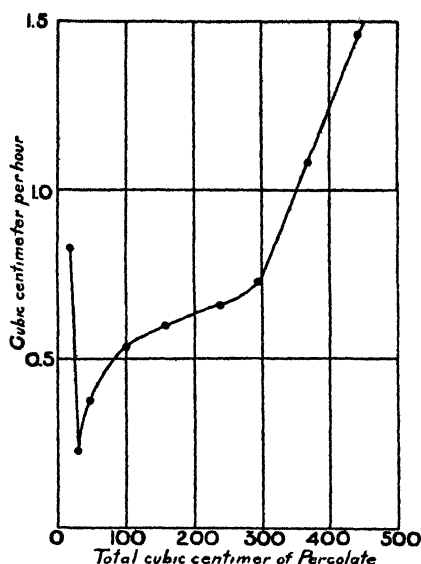


Fig. 3.

TABLE IV.—RATE OF LEACHING IN SOIL FROM FRESNO.

Total cc. percolate.	Cc per hour.
20	0.83
31	0.23
49	0.38
101	0.54
159	0.60
238	0.66
295	0.73
368	1.08
443	1.46

be seen that at first there was a rapid fall in the rate, and then as percolation proceeded with the formation of channels and an increase in the flocculation due to the alkali there is an increase in the rate of percolation, becoming quite regular after about 300 cc. had passed through the soil. It is believed that these changes in the physical condition of the soil as affecting percolation in these experiments are very helpful in showing what may be expected in field practice, although it must be remembered that the intermittent leaching to which the soil is subjected in the field should be more effective than the laboratory results, in so far at least as respects the volume of water required.

In Table V are given the data obtained from the leachings of the Fresno soil, which are also shown in Figs. 4 and 5.

TABLE V.—EXPERIMENTAL DATA FROM FRESNO SOIL.

Time in hours.	Volume of percolate passed.	Conductivity of successive portions of percolate $\times 10^3$ . $t = 25^\circ\text{C}$	Concentration of successive portions of percolate in parts per million of solution.			Total grams constituents leached from 100 grams of soil.		
			CO <sub>2</sub> .	HCO <sub>3</sub> .	Cl.	CO <sub>2</sub> .	HCO <sub>3</sub> .	Cl.
24	20	.....	...	1,514	352	.....	0.0303	0.0070
72	31	.....	...	4,125	961	.....	0.0757	0.0176
120	49	.....	...	2,860	489	.....	0.1268	0.0264
216	101	7.87	81	1,370	101	0.0042	0.1981	0.0317
312	159	3.31	45	475	0	0.0068	0.2256	
432	238	2.37	23	297		0.0086	0.2489	
510	295	1.603	12	206		0.0092	0.2606	
578	368	1.243	12	137		0.0100	0.2706	
630	444	0.842	3	112		0.0102	0.2791	
679	514	0.680	1	105		0.0103	0.2865	
724	572	0.59	0	79			0.2911	
791	656	0.52		73			0.2972	
839	724	0.53		67			0.3017	
916	833	0.49		64			0.3087	
964	912	0.401		55			0.3131	
1,014	1,000	0.366		33			0.3160	
1,061	1,083	0.361		33			0.3187	
1,110	1,162	0.351		33			0.3214	
1,157	1,230	0.376		43			0.3242	
1,229	1,345	0.417		42			0.3291	
1,301	1,459	0.400		42			0.3340	
1,357	1,558	0.370		37			0.3376	
1,424	1,667	0.334		27			0.3406	
1,472	1,744	0.307		21			0.3422	
1,523	1,829	0.312		19			0.3437	
1,569	1,905	0.283		15			0.3449	
1,643	2,017	0.296		12			0.3462	
1,694	2,104	0.293		15			0.3475	
1,742	2,185	0.293		18			0.3490	
1,790	2,271	0.292		18			0.3506	
1,862	2,393	0.235		15			0.3524	
1,934	2,513	0.209		15			0.3542	
2,006	2,626	0.202		15			0.3559	
2,198	2,856	.....		17			0.3598	
2,318	3,061	.....		18			0.3635	
2,438	3,291	0.362		18			0.3677	
2,630	3,575			25			0.3745	
2,745	3,756			15			0.3773	

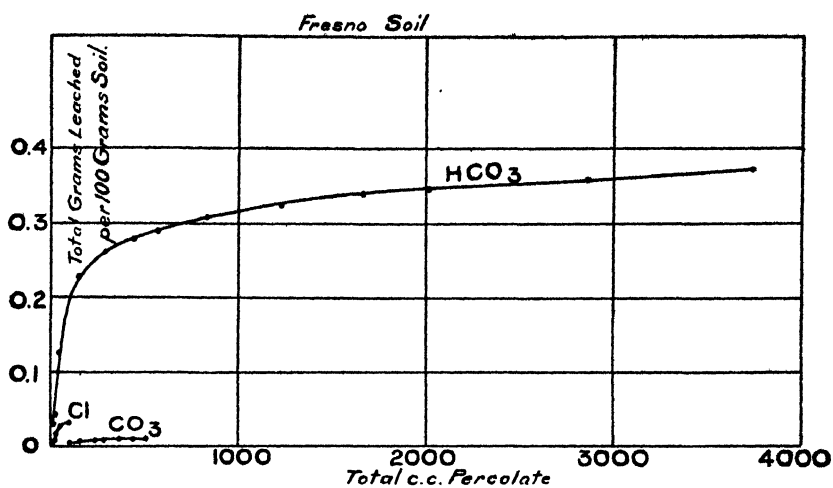


Fig. 4.

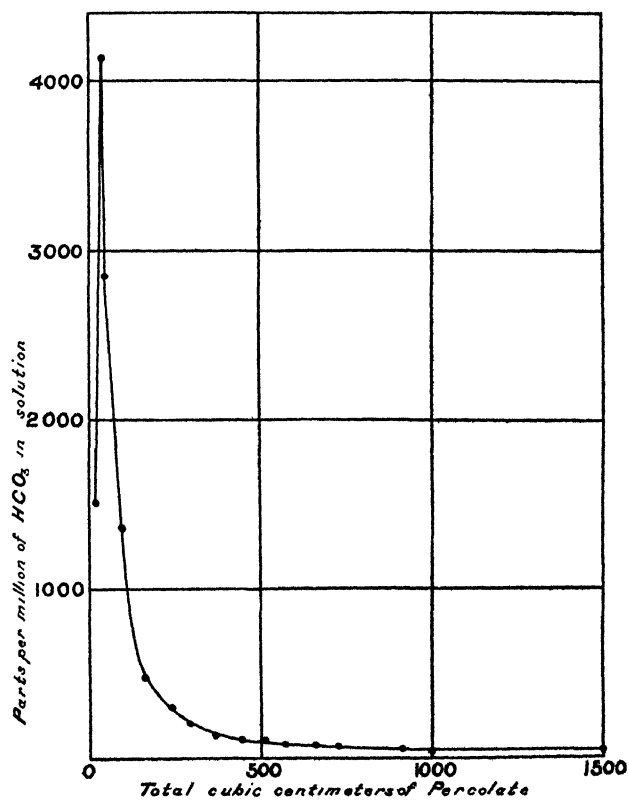


Fig. 5.

It will be observed that in general the results are very similar to those obtained with the heavier soil from Yakima, but, as might reasonably be expected, the soluble salts disappear more rapidly from the lighter soil. It will be interesting to observe also that in the case of the Fresno soil the curve for chlorides (Fig. 4) lies above that for normal carbonates while the reverse is the case with the Yakima soil (Fig. 1). This might seem to illustrate a selective absorption, which soils undoubtedly possess, but nothing of the kind can be predicted in this case, since the Yakima soil probably contained, initially, much more normal carbonates than did the Fresno sample, while both contained approximately the same amounts of chlorides. It will be further observed that the later leachings, while approaching a constant composition with respect to bicarbonates, are more dilute than in the case of the heavier Yakima soil, indicating a higher absorptive power in the latter.

*The Extraction of Soluble Salts from Soils.*—It will be observed that the leachings from the two soil samples here described has resulted in the removal of larger total amounts of soluble salts than the standard method of analysis shows to be originally present. The amounts of carbonates removed by the leaching process agrees with the amounts found present by digesting the soil with five times its weight of water even within the limits of experimental error. In the case of normal carbonates, the continuous leaching as compared with the digestion used in the analytical procedure, showed slightly more in the Yakima soil and somewhat less in the Fresno sample. The differences are, however, so small as to be quite possibly ascribed to analytical errors, but it should be remembered that the addition of much water has the effect of converting a part of the normal carbonates into bicarbonates, and it is in respect to this constituent that the leaching process yields much higher results than does the empirical method employed in the analytical procedure which cannot take proper cognizance of absorption effects. The results on the whole indicate that the analytical procedure, with its known inherent defects, nevertheless gives a very fair idea of the soluble constituents of the soil, where the generally impracticable method of leaching cannot be employed.



## SUMMARY.

In the foregoing pages results have been presented which indicate the following conclusions:

(1) Neutral salts such as the chlorides in the presence of carbonates can be comparatively readily and completely leached from the soil.

(2) With continued leaching of soils containing "black alkali" there is an increase in the rate at which percolation takes place, due probably to the reduction of the amount of alkali present and its effect on the physical structure of the soil.

(3) With continued leaching there is a comparatively rapid reduction of normal carbonates in the soil water, due in large measure to conversion into bicarbonates.

(4) Bicarbonates are rapidly removed at first and then continue to be slowly removed in the soil water in very small amounts, diminishing so slowly as to be practically constant for an indefinite period.

(5) Soils containing "black alkali" can be reclaimed by leaching, but the time and the amount of water required are probably much greater than in the case of "white alkali."

BUREAU OF SOILS,  
U. S. DEPARTMENT OF AGRICULTURE,  
WASHINGTON, D. C.

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THE CRYSTALLINE SUBSTANCES OF PRICKLY ASH BARK.<sup>1</sup>

BY H. M. GORDIN.

Received August 11, 1906.

THE discovery of a crystalline substance in northern prickly ash (*Xanthoxylum fraxineum*, s. *X. Americanum*) is due to E. Staples.<sup>2</sup> The same crystals were later isolated by J. U. Lloyd<sup>3</sup> and more fully examined by G. Eberhardt.<sup>4</sup> To this substance the name of xanthoxylin (xanthoxyline) was given by Staples.

Another crystalline substance was isolated by G. Colton<sup>5</sup> from southern prickly ash (*Xanthoxylum Carolinianum*, s. *X. Clava-Herculis*) and was shown by Eberhardt<sup>6</sup> to be different from the

<sup>1</sup> A preliminary report of this work was read before the A.Ph.A. in 1903.

<sup>2</sup> Am. J. Pharm. 1829, 163.

<sup>3</sup> Ibid. 1890, 229.

<sup>4</sup> Ibid. 1890, 231.

<sup>5</sup> Ibid. 1890, 191.

<sup>6</sup> Loc. cit.

one contained in the northern variety of the drug. This substance, too, was named xanthoxylin.

Still another substance, also named xanthoxylin by its discoverer, was isolated by Stenhouse<sup>1</sup> from Japanese pepper (*Xanthoxylum piperitum* DC.).

The xanthoxylin of Stenhouse is isomeric with cantharidin and seems to be entirely different from either of the crystalline principles contained in the prickly ash barks.

In order to avoid confusion I propose to retain the name xanthoxylin for the substance isolated by Stenhouse from Japanese pepper, and to designate with the name xanthoxylin N the crystalline principle first obtained by Staples from northern prickly ash, and with the name xanthoxylin S the crystalline principle of southern prickly ash.

#### XANTHOXYLIN N.

Among the many substances which accompany xanthoxylin N in the northern prickly ash bark are a considerable amount of fixed oil, in which the xanthoxylin N seems to be very easily soluble, and an amorphous wax-like substance also easily soluble in the oil and in hot alcohol, but difficultly soluble in cold alcohol.

As xanthoxylin N is also easily soluble in hot, but difficultly soluble in cold alcohol, it is quite difficult to isolate xanthoxylin N in perfect purity by simple recrystallization from this solvent even if recrystallization be repeated several times. As the solubilities of xanthoxylin N and of the waxy substance in other solvents also seem to be very much alike, recrystallization from other solvents, too, is very unsatisfactory and connected with great waste of material. This accounts for the small yield obtained by previous investigators.

A preliminary examination of some pure xanthoxylin N obtained from a previous batch by Staple's method showed that, while xanthoxylin N is almost insoluble in cold water and only difficultly soluble in cold alcohol, it is extremely easily soluble in cold alcohol containing a few per cent. potassium hydroxide. Such a solution of xanthoxylin N in alcoholic potassium hydroxide can be diluted with water to any extent without causing the slightest turbidity even after standing for several months. If excess of mineral acid or acetic acid be added to the alkaline

<sup>1</sup> Ann. 89, 257; 104, 236.

solution, the xanthoxylin N, particularly when not quite pure, separates out as an oily liquid, but if the alkaline liquid be saturated with carbon dioxide the xanthoxylin N separates out unchanged and crystalline provided it had not been boiled for some time with the alcoholic solution of the alkali.

Making use of this behavior of xanthoxylin N, the following method seems to be the best for its isolation.

The powdered northern prickly ash bark is exhausted with cold benzene and, after the solvent is distilled off completely, the oily residue is mixed with an equal volume of 5½ per cent. solution of potassium hydroxide in alcohol. After standing for three or four hours the liquid is diluted with an amount of water equal to double the amount of alcohol taken and, after thorough shaking, transferred to a separating funnel. On standing over night a dark layer containing most of the xanthoxylin N dissolved in the alkaline liquid settles at the lower part of the separating funnel while a yellow oil floats on the surface. The alkaline liquid is drawn off and saturated with carbon dioxide. At first the liquid becomes turbid but after a while beautiful shining crystals commence to appear which look very pretty in the dark liquid. The crystals were collected after a few days' standing of the liquid and, after thorough washing with water, dried and weighed. The crude xanthoxylin N obtained by this method amounted to 3.5 per cent.

For purification the xanthoxylin N had to be recrystallized eight times, using animal charcoal in the last recrystallizations, before the melting-point remained constant.

Xanthoxylin N forms dazzling white needle-shaped crystals. It is extremely easily soluble in benzene, chloroform and hot alcohol. It is a little less soluble in cold acetone and less yet in ether. It is soluble in 49 parts of cold alcohol and about 25,000 parts of cold water. It melts at 132.5° to a clear yellowish liquid which does not re-solidify on cooling for about two hours. At 110° it assumes a yellowish tint but becomes white again on cooling.

A solution of xanthoxylin N in ethyl or methyl alcohol is colorless. Upon the addition of potassium hydroxide the alcoholic solution becomes yellow but the color disappears upon neutralizing the alkali with an acid. A saturated solution of xanthoxylin N in water has no color if kept protected from the air. Exposed

to the air or upon addition of alkali, the aqueous solution soon assumes a bluish fluorescence. The fluorescence is intensified by addition of potassium hydroxide. Addition of about 10 per cent. alcohol or a few drops of dilute acid destroys the fluorescence.

In presence of potassium hydroxide, xanthoxylin N is very easily soluble in cold alcohol but solution is not effected immediately.

On covering 1 gram xanthoxylin N with 10 cc. of a 5 per cent. solution of potassium hydroxide in alcohol it takes about an hour to dissolve all of the substance. On evaporating the alcohol from such a solution after diluting it with four times the amount of water, the liquid assumes a dark yellow color but no xanthoxylin N separates out on standing if the solution be protected from the carbon dioxide of the air.

Xanthoxylin N is tasteless in aqueous solution and has a very slight pricking taste in alcoholic solution.

It is optically inactive.

Cold aqueous potassium hydroxide does not affect xanthoxylin N. When boiled for a long time with a 10 per cent. solution of the alkali it very slowly goes into solution, forming a dark yellow liquid from which it is reprecipitated unchanged by a current of carbon dioxide.

Sulphuric acid colors xanthoxylin N red. On digesting xanthoxylin N in cold sulphuric acid till it is dissolved and then throwing the red solution into much water the xanthoxylin N separates out unchanged as shown by melting-point and general behavior. If xanthoxylin N be digested over night with sulphuric acid at a temperature of  $80^{\circ}$  and the dark red solution then thrown into water a resinous precipitate separates out which is easily soluble in alkalies and alkaline carbonates but difficultly soluble in barium hydroxide.

The formula of xanthoxylin N given in the preliminary report was corroborated by new analysis.

The analysis gave C, 69.65, 69.64, 69.89 and 69.93; H, 5.33, 5.53, 5.39 and 5.70. Calculated for  $C_{18}H_{14}O_4$ : C, 69.73; H, 5.47.

A molecular weight estimation by the lowering of the freezing-point, using benzene as solvent, gave 225, 254, 273 and 289. Calculated for  $C_{18}H_{14}O_4$ , 258.14.

Tested by Zeisel's method xanthoxylin N was found to contain

one methoxyl group. In carrying out the method it was found that when hydriodic acid alone is used the substance becomes one solid lump which does not break up during the whole operation, hence the results obtained are about 1 per cent. too low; but if the substance is first dissolved in 8 cc. of warm glacial acetic acid and the solution then mixed with 10 cc. hydriodic acid (sp. gr. 1.7) the results are very fair.

Analysis gave 11.47 and 11.46  $\text{CH}_3\text{O}$ . Calculated for  $\text{C}_{14}\text{H}_{11}(\text{CH}_3\text{O})\text{O}_8$ , 12.03  $\text{CH}_3\text{O}$ .

*Hydrated Xanthoxylin N Dibromide*,  $\text{C}_{15}\text{H}_{14}\text{Br}_2\text{O}_4\cdot\text{H}_2\text{O}$ .—The presence of a double binding in xanthoxylin N is shown by the absorption of one molecule of bromine by a molecule of xanthoxylin N. Five grams of xanthoxylin N were dissolved in 30 cc. glacial acetic acid and a 20 per cent. solution of bromine in the same solvent then added drop by drop till the slightly yellowish tint, which appears after the addition of the first drop of the bromine solution, changes to a decided red. About 3.2 grams of bromine were consumed and no evolution of hydrobromic acid could be noticed. The reddish liquid was then thrown into about 700 $\frac{1}{2}$  cc. of very cold water with constant stirring. The white precipitate which separated was thoroughly washed with water and after drying on porous plates recrystallized from a mixture of acetone and alcohol. The brominated xanthoxylin N crystallizes in white warts, melting at  $171^\circ$  with effervescence. Analysis of the compound showed that in the treatment with bromine under the above conditions xanthoxylin N takes up besides two atoms of bromine one molecule of water. This water cannot be removed either by keeping the brominated compound in vacuum over sulphuric or by heating it to  $110^\circ$  for three hours.

Analysis gave C, 41.19 and 41.05; H, 3.59 and 3.55; Br, 36.33 and 36.94. Calculated for  $\text{C}_{15}\text{H}_{14}\text{Br}_2\text{O}_4\cdot\text{H}_2\text{O}$ : C, 41.28; H, 3.71; Br, 36.67.

On prolonged exposure to the light the dibromide assumes a yellowish tint. The dibromide is easily soluble in cold alcohol and insoluble in water. It is very easily soluble in cold alcohol containing potassium hydroxide and the alkaline alcoholic solution can be diluted with water to any extent.

*Dihydroxanthoxylin N*,  $\text{C}_{18}\text{H}_{18}\text{O}_4$ .—On passing a current of hydriodic acid into a solution of xanthoxylin N in eight times its amount of glacial acetic acid the substance takes up two hydrogen

atoms and separates out as a hard resinous mass upon dilution of the acid liquid with water. After removal of the iodine by the usual methods and recrystallizing repeatedly from hot alcohol the dihydro compound was obtained in white needles melting at 142–143°. The dihydro compound is easily soluble in ether, chloroform, benzene and hot alcohol. It is difficultly soluble in cold alcohol and almost insoluble in water. Towards aqueous and alcoholic potassium hydroxide it behaves like xanthoxylin N itself.

Analysis gave C, 69.31 and 69.05; H, 6.50 and 6.25. Calculated for  $C_{15}H_{18}O_4$ : C, 69.19; H, 6.21.

The dihydroxanthoxylin N, like xanthoxylin N, contains one methoxyl group.

Analysis gave 11.56 and 11.50  $CH_3O$ . Calculated for  $C_{14}H_{18}(CH_3O)_3$ , 11.93  $CH_3O$ .

All attempts to prove the presence of hydroxyl or ketone groups in xanthoxylin N by the usual methods were unsuccessful. In every case the substance was recovered unchanged. The behavior of the substance towards alcoholic potassium hydroxide and subsequent dilution with water would seem to indicate that xanthoxylin N is a lactone. That this is not so is shown by the fact that it does not form a benzoyl compound in alkaline solution.

The experiment was carried out as follows: The xanthoxylin N was dissolved in about six times its amount of pyridine and the solution shaken three hours with a 20 per cent. solution of sodium hydroxide, using an amount of the alkaline solution equal to the amount of pyridine taken. The liquid which became miscible with water was then shaken with benzoyl chloride, after adding some more dilute sodium hydroxide.

The solution was then treated with an excess of carbon dioxide and the precipitate which separated out recrystallized from hot alcohol. It was found to be unchanged xanthoxylin N as shown by its melting-point and general behavior.

Xanthoxylin N does not behave like an anhydride of a monobasic acid as it does not form an anilide when treated with aniline.



The experiment was carried out by dissolving 0.5 gram xanthoxylin and 0.5 gram aniline in 10 cc. of hot alcohol and setting

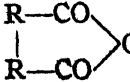
<sup>1</sup> Menshutkin and Wassiliew: J. russ. chem. Ges. 1889, 192.

the liquid aside over night. Most of the xanthoxylin N crystallized out unchanged as was shown by its melting-point and the absence of nitrogen by Lassaigne's test. On the other hand, towards other reagents xanthoxylin N acts like a monobasic acid.

When xanthoxylin N is dissolved in an excess of standardized solution of potassium hydroxide in methyl alcohol and, after dilution with water, the excess of alkali titrated with standard acid, no acid properties are indicated by methyl orange, but if phenolphthalein be used as indicator the xanthoxylin N behaves like a monobasic acid. 1.0127 grams xanthoxylin N neutralized 7.9 cc. N/2 potassium hydroxide. Calculated for  $C_{16}H_{14}O_4$  as a monobasic acid, 7.7 cc. If the neutralized liquid is set aside in a stoppered flask it turns red again in about an hour. On now adding more standard acid till the red color disappears and setting the liquid aside, it again assumes a red color on standing. This phenomenon is repeated till an amount of acid is added which is equivalent to the amount of alkali used. The whole operation occupied about three days. Hence xanthoxylin N shows the phenomenon of slow (abnormal) neutralization like some pseudo-acids studied by Hantzsch.

Towards resorcinol xanthoxylin N behaves like an anhydride of a dibasic acid, giving the phthalein reaction with great brilliancy. On heating xanthoxylin N with four times the amount of resorcinol and a small amount of fused zinc chloride to  $150^\circ$  till a drop of the melt becomes soluble in cold dilute potassium hydroxide (about two hours), dissolving the melt in dilute alkali and then adding an excess of acetic acid, a yellow precipitate is formed which is very little soluble in water or dilute acids but dissolves in dilute alkali with intense blue fluorescence. A blank experiment with resorcinol alone showed that the phthalein reaction was due solely to the xanthoxylin N, as the resorcinol melt gives with alkali only a green fluorescence but no yellow precipitate upon addition of acids.

It follows from these experiments that of the four oxygen atoms of xanthoxylin N the function of only one is established with certainty as belonging to a methoxyl group. As to the other three oxygen atoms it is as yet impossible to say whether they are

present in the form of a  $(R.CO)_2O$  group, or a  group

or in some other form. Further work which I have in hand will, I believe, clear up the subject.

#### XANTHOXYLIN S.

The xanthoxylin S existing in southern prickly ash seems to be nearly related to the xanthoxylin N of the northern bark. Analysis seems to indicate that it is the next lower homologue of xanthoxylin N, *i. e.*, it contains  $\text{CH}_2$  less than xanthoxylin N.

Xanthoxylin S does not behave towards potassium hydroxide and carbon dioxide like xanthoxylin N, and the method used for the separation of the latter from the oil cannot be used for the separation or purification of xanthoxylin S. As the xanthoxylin S does not seem to be affected by boiling alcoholic potassium hydroxide, it might be possible to separate it from the oil by saponifying the oil and shaking out with benzene or ether. I intend to try this method later on. For the present, I have obtained a small amount of the xanthoxylin S in the following way:

The powdered southern prickly ash was exhausted with benzene, the latter distilled off completely, and the oily residue mixed with twice its volume of petroleum ether. On standing over night a considerable amount of a crystalline sediment separated out. The crystals were taken up with cold ether, the ethereal solution filtered, the ether distilled off, and the residue recrystallized repeatedly from hot alcohol.

Thus obtained the crystals were snow-white, and melted at  $119-120^\circ$ .

Analysis gave the following results:

(1) 0.28585 gram substance gave 0.71587 gram  $\text{CO}_2$  and 0.1429 gram  $\text{H}_2\text{O}$ .

(2) 0.1150 gram substance gave 0.2901 gram  $\text{CO}_2$  and 0.0575 gram  $\text{H}_2\text{O}$ .

Calculated for  $\text{C}_{14}\text{H}_{12}\text{O}_4$ : C, 68.81; H, 4.96. Found: C, 68.54; H, 5.62.

No methoxyl group could be found by Zeisel's method. The xanthoxylin S is possibly an alcohol or a phenol of which xanthoxylin N is the methyl ether. The formula of xanthoxylin S could then be written  $\text{C}_{14}\text{H}_{11}(\text{OH})\text{O}_3$ , and that of xanthoxylin N,  $\text{C}_{14}\text{H}_{11}(\text{O.CH}_3)\text{O}_3$ . The figures obtained by the elementary analysis of xanthoxylin S would also correspond to the formula



$C_{21}H_{18}O_6$ . An estimation of the molecular weight by the freezing-point method with benzene as solvent, gave as an average 326. The formula  $C_{14}H_{12}O_4$  gives 244.12; the formula  $C_{21}H_{18}O_6$  gives 366 for the molecular weight. A study of other derivatives will be required for the establishing of the exact formula of xanthoxylin S. This work is to be continued.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## INVESTIGATIONS ON THE PROPERTIES OF WHEAT PROTEINS.

BY JOSEPH S. CHAMBERLAIN.

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### I. THE SEPARATION OF THE PROTEINS.

THE proteins of wheat according to the work of Osborne and Voorhees,<sup>1</sup> are five in number, *viz.*, gliadin, glutenin, an albumin, a globulin and proteose. The first of these, gliadin, is soluble in 70 per cent. alcohol. Glutenin is insoluble in alcohol, and together with gliadin constitutes about 80 to 85 per cent. of the total proteins of the wheat. The other three proteins, *viz.*, the albumin, the globulin and the proteose are soluble in dilute salt solutions and together constitute about 15 to 20 per cent. of the total proteins present.

This separation of the proteid substance of wheat into these five individual proteins is not accepted by all who have worked upon the problem, *e. g.*, F. Kutscher<sup>2</sup> claims, from a study of the cleavage products, that there are but three proteins in wheat, *viz.*, gluten casein, corresponding to Osborne and Voorhees' glutenin, gliadin, readily soluble in 60 per cent. alcohol, and gluten fibrin, slightly soluble in 60 per cent. alcohol. Ritthausen<sup>3</sup> had previously distinguished four proteins, one insoluble in alcohol, gluten casein, and three soluble in alcohol, *viz.*, gliadin, gluten fibrin and mucedin. Kutscher<sup>4</sup> claims, from a study of the products of hydrolysis, that mucedin and gliadin are the same.

<sup>1</sup> Am. Ch. J. 15, 392 (1893).

<sup>2</sup> Z. physiol. Chem. 38, 111 (1903).

<sup>3</sup> "Die Eiweisskörper der Getreidearten, Hülsenfrüchte und Oelsamen" (Bonn, 1872, Dissert.).

<sup>4</sup> Loc. cit.

Fleurent<sup>1</sup> claims three different proteins present in wheat gluten, and König and Rintelen<sup>2</sup> agree with Ritthausen that there are four. One explanation of this difference of opinion is, that some of the above investigators worked with wheat gluten alone, while others worked with the wheat itself. As will be shown later on, wheat gluten is not of uniform composition, unless prepared by exactly the same methods and under the same conditions, nor does it contain all of the proteins of the wheat.

Without going more into detail in regard to the views of these and other writers on this subject the author wishes to speak of some results that have been obtained in an effort to make a quantitative separation of the proteins of wheat. Osborne and Voorhees<sup>3</sup> state, as the general quantitative result, that the amounts of the different proteins in wheat are:

TABLE I.

	Protein. Per cent. of wheat.	Protein. Per cent. of total proteins.
Glutenin .....	4.428	40.25
Gliadin .....	3.936	35.78
Globulin .....	0.625	5.68
Albumin .....	0.621	5.64
Proteose .....	0.322	2.93
H <sub>2</sub> O washings.....	1.076	9.78
Total.....	11.009	100.06

## ACTION OF HOT ALCOHOL.

It is practically impossible to extract a flour with a salt solution and then, after filtering it, to extract the residue with alcohol, because of the difficulty of filtering off the salt solution completely and the effect of the presence of a small amount of salt on the solubility of the alcohol-soluble proteins. The following table gives results obtained when the flour was extracted directly with 70 per cent. alcohol, and examination was made to see if hot alcohol would dissolve out more protein than cold. In this and the following tables the results are the averages of a series of determinations in each case.

<sup>1</sup> Ann. Agron. 1898, 371.

<sup>2</sup> Z. Nahr. Genussm. 8, 401, 721 (1904).

<sup>3</sup> Loc. cit.

TABLE II.

	Protein. Per cent. of flour.	Protein. Per cent. of total proteins.
Cold alcohol on air-dry flour.....	7.47	56.80
Hot alcohol on air-dry flour.....	7.32	54.43
Cold alcohol on dry flour.....	4.58	34.82

These results show that the use of hot alcohol has a diminishing effect due, no doubt, to the coagulating action of the hot solution and its effect on the solubility of the proteins. If, also, the flour is dried before the extraction is made, the effect on the solubility is even greater and the difference between alcohol-soluble proteins extracted by cold alcohol, on air-dry flour and on dried flour, is about 20 per cent. of the total proteins present. Some investigators have used, for extracting gliadin, flour which had been extracted with ether. If this could be accomplished without first drying the flour by means of heat it might do, but otherwise it would be liable to the same errors as the hot extraction.

EFFECT OF DIFFERENT AMOUNTS OF FLOUR, IN PROPORTION TO THE  
EXTRACTING LIQUID, ON THE AMOUNT OF PROTEIN EX-  
TRACTED.

Osborne and Voorhees in their work used large quantities of wheat or flour and determined the amount of protein by weight, after purifying it by fractional precipitation and drying. Taking their analysis of the pure proteins as correct and using, therefore, the factor 5.68 or 5.7, the amounts of protein extracted in these investigations were determined by nitrogen determinations, kindly made by Mr. T. C. Trescott, of the Bureau of Chemistry. Repeating as nearly as was possible the operations of Osborne and Voorhees, and determining the nitrogen in the numerous filtrates and residues, calculating all to the basis of the original dry flour, the results in Table III were obtained. In the first column are the results obtained when relatively large amounts of flour were used. In these cases 1,000 grams of flour were extracted with 4,000 cc. of 70 per cent. alcohol for twenty-four hours, and subsequent extractions were made, using 2,000 cc. alcohol each time until the total amount of alcohol used equaled 10,000 cc. In the second column are the results obtained when relatively small amounts of flour were used. In these cases 2 to 4 grams of flour were extracted once with 100 cc. of 70 per cent. alcohol for twenty-four hours.

TABLE III.—PROTEIN IN PER CENT. OF TOTAL PROTEINS.

	Using large amounts of flour.	Using small amounts of flour.
Direct extraction with alcohol.....	43.56	47.15
Extraction with salt solution after preceding extraction with alcohol.....	5.98	5.51
	49.54	52.66
Direct extraction with salt solution.....	13.54	16.26
Extraction with alcohol after preceding ex- traction with salt solution.....	32.71	29.26
	46.25	45.52

Thus we see that the amount of protein extracted depends upon the relative amounts of solvent and solute. Several extractions, aggregating seventy-two hours, in addition to the twenty-four hour extraction, failed to yield more than a mere trace of protein when the small amounts of substance were used, whereas when large amounts were used, four separate extractions were made and the last extraction yielded about 7.0 per cent. of the total proteins extracted, and in another case about 1.5 per cent.

TABLE IV.

	Protein. Per cent. of flour.	Protein. Per cent. of total proteins.
Direct extraction with alcohol...	7.47	56.80
Extraction with salt solution after preceding extraction with alcohol.....	0.57	4.33
	8.04	61.13
Direct extraction with salt solu- tion.....	2.18	16.57
Extraction with alcohol after preceding extraction with salt solution .....	5.50	39.26
	7.68	55.83

As is shown by both Tables III and IV, the amounts of both the alcohol-soluble protein and the salt solution-soluble proteins are different when the wheat is extracted directly and when it has been previously extracted with the other solvent. In the case of the alcohol extraction preceded by the extraction with salt solution, this difference is undoubtedly due to the fact that the salt retained in the extracted flour or wheat affects the solubility of the alcohol-soluble proteins. When the salt solution extraction was preceded by the alcohol extraction, it would seem, that, by air-drying the sample after the alcohol extraction, if the alcohol had no solvent effect upon the salt solution-soluble proteins, its effect would disappear with its evaporation, and we should obtain by the following salt solution extraction the same amount of protein

as we do from a direct extraction with salt solution. But this is not the case, as is seen from Table IV, for we obtain, by direct extraction with salt solution, 16.57 per cent. of the total proteins, whereas after extracting with alcohol we obtain only 4.33 per cent. This can mean only one thing, *viz.*, that alcohol dissolves, with the gliadin, a large part of the albumin, globulin and proteose, which are soluble in salt solutions. That it does not extract all is shown by the fact that extraction with salt solution, after alcohol extraction, always yields protein material, usually about 4 or 5 per cent. of the total. Osborne and Voorhees found globulin to be about 5.6 per cent. of the total proteins, and it seems probable that dilute alcohol (70 per cent.) dissolves out, with the gliadin, the albumin and proteose and leaves the globulin. This is shown also from the following data in Table V. In this table are given the results obtained from a series of determinations in which both the alcohol extraction and the salt solution extraction were made directly on the flour, and, also, each extraction was made on flour previously extracted with the other solvent. In addition the salt solution extract itself was extracted with alcohol in the following manner: Alcohol of 95 per cent. was added to the salt solution extract in such quantity as to make a resulting alcohol equal to 70 per cent. The precipitate formed was then filtered off and the protein remaining in solution in the alcohol was determined.

TABLE V.—PROTEIN IN PER CENT. OF TOTAL PROTEINS.

Direct extraction with alcohol .....	56.73
Direct extraction with salt solution.....	20.80
Extraction with alcohol after preceding extraction with salt solution...	41.20
Extraction with salt solution after preceding extraction with alcohol...	4.92
Extraction of the salt solution extract with alcohol.....	12.70

In this table, as in Table IV, the results show that direct extraction with 70 per cent. alcohol dissolves out, not only the protein gliadin, but also a portion of the proteins characterized as salt solution-soluble, and that this portion may be extracted by alcohol, either directly from the flour or from the salt solution extract itself.

From this portion of the work we can conclude, therefore:

- (1), For the proper extraction of the proteins of wheat by means of alcohol, cold 70 per cent. alcohol should be used directly upon the air-dry wheat or flour. Relatively large amounts of solvent, in proportion to the flour, should be taken, *viz.*, 2 to 4 grams flour

per 100 cc. alcohol, and the extraction continued for twenty-four hours. Either hot alcohol or dry flour gives abnormal results.

(2) The same conditions of extraction should be observed in using the salt solution. The author has found that 5 per cent. potassium sulphate solution extracts practically the same as 10 per cent. sodium chloride and is better in practice, because it avoids the evolution of hydrochloric acid gas when digested in the Kjeldahl operation. Four to 6 grams of flour are taken per 100 cc. of solvent and the extraction continued for twenty-four hours with frequent or continued shaking.

(3) In the extraction with alcohol there is extracted, with the alcohol-soluble protein, gliadin, a large part of the salt solution-soluble proteins, probably the albumin and proteose. Corrections for such overlapping of the extractions must be made whenever a quantitative separation of the proteins is attempted.

(4) As recommended by the author, in the Association of Official Agricultural Chemists,<sup>1</sup> the separation of the proteins of wheat into more than two groups, *viz.*, (1) alcohol-soluble, and (2) alcohol-insoluble, seems unwarranted, both because of the difficulty of making a further quantitative separation and because of the indefinite value of such separation.

## II. WHEAT GLUTEN.

The proteid bodies of the wheat grain are especially interesting and important because it is to them that wheat flour owes its exceptional adaptability to the making of bread.

Before the proteins of wheat were known or studied as individuals it was known that practically all of them were present in what is termed wheat gluten. This gluten is obtained by the simple mechanical process of washing away starch and soluble constituents by kneading a ball of dough in the hand in a small stream of water. The residue is a tough elastic mass rich in nitrogen and containing the larger part of the proteid constituents.

The determination of the amount of this gluten, either wet or dry, or both, has long been considered as of value in judging the character of wheat and flour for bread-making purposes. The determination is, however, one in which so many errors are involved that it seems hardly to be of value as a chemical factor

<sup>1</sup> A. O. A. C. Proceedings, 1903, 1904. Bull. 81, 118, and Bull. 90, 121, 127, Bur. Chem., U. S. Dept. Agr.

when the corresponding factor of total proteins, by nitrogen determination, is so reliable and easy to carry out.

It is for the purpose of showing some of the errors in the ordinary gluten determination that the following facts have been brought together from the results obtained by the author during the last year or so.

It has been admitted by those who have worked on this method that differences in temperature of wash-water, its salt content and the time and manner of manipulation all have a strong influence in varying the final result of the amount of gluten. Fleurent,<sup>1</sup> the most ardent advocate of the value of the gluten determination, claims that by using water of a certain arbitrary salt content and exact methods as to time and manner of washing, uniform results may be obtained.

It is true that concordant duplicates can be obtained by any one after becoming thoroughly acquainted with the operation so as to be able to duplicate conditions exactly. But even though the results are concordant, do they mean anything, or if so, do they mean more than other more reliable determinations?

F. A. Norton<sup>2</sup> has studied the composition of crude gluten and the relation between gluten and total proteins, by nitrogen determination. His results are based on the analysis of the gluten itself and the determination of non-proteid material in it.

The following results are based on an examination of the proteid material lost in the process of washing out the gluten and contained in the wash-water therefrom. It will be seen that the data and conclusions obtained in this investigation are in agreement with those obtained by Norton.

#### THE EFFECT OF PHYSICAL CONDITION OF THE SAMPLE ON THE DETERMINATION OF GLUTEN.

The average of the determinations made on some fifty samples of wheat, when simply ground as whole wheat, give an amount of dry gluten about 2.31 per cent. lower than the total proteins calculated from total nitrogen multiplied by 5.7. If we allow for the amount of amino bodies present, this excess of total proteins over dry gluten will be reduced by about 1.0 per cent. or

<sup>1</sup> Ann. chim. anal. 10, 129, 195, 238, 276, 309 (1905); Compt. rend. 140, 99 (1905).

<sup>2</sup> This Journal, 28, 8 (1906).

less. If the samples worked with are the finest patent flours the results for dry gluten will average nearly as much in excess of total proteins as the others did below:

TABLE VI.

	Total nitrogenous bodies.	Amino bodies.	Total proteins.	Dry gluten.
Flour <sup>1</sup> .....	13.07	.....	13.07	14.30
Difference ..	.....	.....	.....	+ 1.23
Whole wheat.....	10.26	1.26	9.00	7.95
Difference.....	.....	.....	.....	— 1.05

The amount of true proteid material in the two classes of glutes is, however, nearly the same.

TABLE VII.

	Nitrogen. Per cent.	Proteins. Per cent. (N × 5.7).	Non-proteins. Per cent.
Whole wheat gluten .....	13.11	74.72	25.28
Patent flour gluten.....	13.54	77.17	22.83
Theoretical .....	17.60	.....	.....
Average.....	.....	75.94	24.06

These facts can readily be understood if we consider the physical condition of the material, which makes it easy for a considerable loss of proteins, mechanically, in washing out the whole wheat so as to wash away all particles of bran, and the corresponding smaller loss when patent flour is used, the amount of non-proteins retained by the gluten being in one case approximately the same as in the other.

An examination of the wash-water from whole wheat, after the gluten has been obtained, shows us where the loss of proteins occurs. Collecting all wash-water, after allowing it to pass through a bolting-cloth sieve to retain bran, and later allowing the filtrate to settle for twenty-four hours until the greater part of the starch had settled and the supernatant liquid could be siphoned off, and analyzing all these portions for nitrogen, gave the following results:

TABLE VIII.

	Nitrogen compounds calculated as protein. Per cent.	Per cent. of the total nitrogen compounds.
Filtrate.....	2.16	21.23
Residue { Starch.....	0.51	5.03
{ Bran.....	1.71	16.76
Total .....	4.38	43.02

<sup>1</sup> Bull. 70, Bur. Plant Ind., U. S. Dept. Agr.



The loss of nitrogenous compounds, calculated as protein, in the washing out of gluten is, therefore, equal to 4.38 per cent., or 43.02 per cent. of the total nitrogenous compounds present. If we allow for the amino bodies found to be present, by the ordinary Stutzer method, we have, considering that all amino compounds are in the filtrate from the gluten washing, the following results:

TABLE IX.

	Per cent. of wheat.	Per cent. of total proteins.
Proteins in gluten (13.11 per cent. N).	5.81	64.56
Proteins in washings {		
Filtrate .....	0.91	10.11
Starch residue..	0.51	5.66
Bran residue....	1.71	19.00
	<hr/>	<hr/>
	8.94	
Total proteins (Alb. N $\times$ 5.7) .....	9.00	99.33
Amino compounds (amino N $\times$ 4.25) .	0.93	
	<hr/>	
Total N. comp.....	9.93	

We thus see that the gluten is only about 76 per cent. pure protein, and that of the total proteins present in wheat about 65 per cent. is found in the gluten and 35 per cent. in the washings.

From the average composition of wheat bran and shorts, (2.65 per cent. nitrogen), and the fact that they constitute about 30 per cent. of the wheat, there would be in the bran of the whole wheat, not present in flour, about 34 per cent. of the total nitrogenous compounds present. The loss in nitrogenous compounds during the washing is, as we have seen from Table VIII, 43 per cent., so that, in the washing out of the gluten, there is lost, over and above the nitrogenous compounds present in the bran, about 9.0 per cent. of the total nitrogenous compounds.

Also, we see that in the gluten there is, calculated as per cent. of the total proteins, about 25 per cent. (Table VII) of non-proteins. The difference between the proteins lost in washing, 35 per cent., and the non-proteins present in the gluten, 25 per cent., is, therefore, the absolute difference between the total proteins and the amount of dry gluten. This is equal to about 10 per cent. in favor of the total proteins, making the dry gluten less than the total proteins. This agrees practically with the statements in the preceding paragraph. When gluten determinations are made with flour, however, the loss in bran is nothing and the only loss is in soluble amino compounds, which is so small

in amount as to be practically negligible, and in dissolved and mechanically lost particles of protein, so that the non-proteins in the gluten more than balance the loss of proteins during the washing, and the dry gluten will equal or usually exceed the total proteins calculated from total nitrogen. Another table showing results of a later series of determinations gives practically the same conclusions, though the figures are not exactly the same.

TABLE X.

	Proteins in per cent. of wheat.	Proteins in per cent. of total proteins.
Gluten.....	5.41	59.32
Filtrate.....	2.05	22.47
Starch residue.....	0.63	6.91
Bran residue .....	0.91	10.00
	<hr/>	<hr/>
	9.00	98.70
Total protein ( $N \times 5.7$ ) .....	9.12	

The determination, by the extraction method, described in the preceding part of this paper, of the amounts of the different proteins present in whole wheat, gave as the average of all the samples represented in Tables IX and X the following results:

TABLE XI.

	Proteins in per cent. of wheat.	Proteins in per cent. of total proteins.
Salt solution-soluble proteins.....	2.16	23.68
Gliadin and glutenin.....	6.96	76.31

Comparing Tables IX, X and XI, it will be seen that, calculated as per cent. of total proteins, about 15 per cent. of the proteins gliadin and glutenin, which are the true agglutinating proteins of wheat, are not accounted for in the gluten; and, that, on the other hand, there is present in the washings about 15 per cent. more protein than is represented by the salt solution-soluble proteins of the wheat.

This means that there is lost in the operation of washing out gluten about 15 per cent. of those proteins of which gluten is composed.

The following conclusions seem justified from the preceding facts:

(1) Dry gluten is about 75 per cent. proteins and 25 per cent. non-proteins.

(2) Of the total proteins present in wheat about 60 to 65 per cent. are present in the gluten, and about 35 to 40 per cent. are lost in the washings.

(3) The balance between the non-proteins present in the gluten and the loss of proteins in washing, makes gluten determinations agree roughly with total proteins calculated from total nitrogen, but they will usually fall below with whole wheat and above with flours.

(4) The amount of total proteins present in gluten is about 15 per cent. less than the sum of the gliadin and glutenin determined by extraction of the wheat, and the loss of proteins in washing out gluten is more than equal to the salt solution-soluble proteins. Therefore, the loss of proteins, in the determination of gluten, is at the expense of gliadin or glutenin, the true gluten proteins of wheat.

(5) On account of these losses and errors it would seem that the determination of gluten is not able to yield any information that cannot be gained either from the determination of total proteins or that of the alcohol-soluble and insoluble proteins.

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NOTE.

*Two New Weighing-bottles.*—The weighing-bottles described were devised by the writer some time ago and have been found useful by some of his colleagues and himself. The advantages

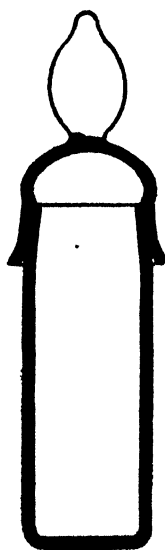


Fig. 1.

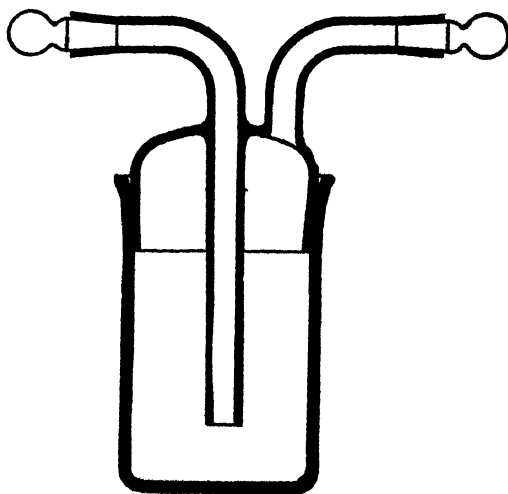


Fig. 2.

of a weighing-bottle with a light cap stopper (Fig. 1) ground on outside are various. In weighing by difference nothing can stick to the ground surfaces, and hence several portions can be weighed out successively without the ground joint having to be cleaned, as is necessary with the ordinary form of stopper. This is of particular advantage in the case of hygroscopic substances, and also prevents the stopper from sticking. When weighing a filter, this can project up to the top of the weighing-bottle and completely fill it. Further, no dust can accumulate between the ground surfaces, and the bottle is easily wiped clean. This weighing-bottle may be obtained in various sizes from C. Desaga in Heidelberg, and from Messrs. A. Gallenkamp & Co., and Messrs. Muller, Orme & Co., in London.

The second kind of weighing-bottle (Fig. 2) is of use in drying substances to constant weight in a current of gas, or in determining water of crystallization, etc. The bottle is heated to the desired temperature in a small air-bath, formed of a large porcelain crucible covered with a piece of asbestos board suitably perforated, and a current of dry gas, if necessary, hydrogen or nitrogen is passed through. These little ground-in stoppers to the gas entry and exit tubes close the bottle tightly and are very convenient. They were introduced by Dr. R. J. Seligman, and are also exceedingly useful for Geissler's potash bulbs, and for calcium chloride drying tubes, and as the ground joint is inside, there is no danger of bits of rubber tubing adhering to the outside of the glass tubes.

LEO FRANK GUTTMANN.

NEW YORK.

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### NEW BOOKS.

THEORIEN DER CHEMIE . . . VON SVANTE ARRHENIUS . . . UEBERSATZT VON ALEXIS FINKENSTEIN Leipzig 1906

This book of VII + 177 octavo pages contains a translation of a course of lectures delivered at the University of California in the summer of 1904. The author had long desired to prepare an account of the development of chemical theories, moved thereto by the fact that recent additions to the science are sometimes regarded, both by their adherents and by their opponents, as something entirely new, with no root or germ in the past; as being the more admirable the more independent they are of the older chemical theories. He hopes to show that in the newer chapters

of theoretical chemistry, the older doctrines have attained a consequent and necessary extension, by the same path as that by which the science has made its advances for a century. Scholars who desire to pull down recent additions to the chemical edifice will learn, thinks the author, that their success would involve in ruin the adjacent walls of the older structure, a result which these scholars regard as neither desirable nor possible. Arrhenius asserts that the material and the workmanship of the chemical builders of the day are worthy of Boyle and Lavoisier and Richter and Dalton. In details, methods of workmanship change, for better tools are available; and in details, the older parts of the edifice undergo an almost unconscious architectural restoration, which brings their aspect into perfect harmony with that of the newer additions.

The great facility with which this adjustment of the older doctrines of chemistry to the more recent takes place is asserted to be the best evidence of the soundness of recent ideas, and the lecturer hopes to prove that the more recent developments of theory sustain this test.

The pages of the little book are readable, suggestive, clear. It would be hard to produce a more valuable short account of chemical theories. The sense of proportion shown throughout is well illustrated by the fact that electrolytic dissociation is treated in less than one-tenth of the whole number of pages.

Even when chemical theory shall have outgrown this treatise, it will still be a valued record of the course of thought pursued by the discoverer of the theory of electrolytic dissociation.

EDWARD W. MORLEY.

THE INFLUENCE OF MOLECULAR CONSTITUTION UPON THE INTERNAL FRICTION OF GASES. By FREDERICK MALLING PEDERSEN. Dissertation. 1906. New York: D. Van Nostrand Co.

After an extensive historical review, the author describes a simple form of apparatus for determining the internal friction of vapors at 100°. At this temperature the coefficient of friction was determined for ten ethers and from the values thus found the author calculates the molecular volumes by means of the formula of L. Meyer. These molecular volumes agree roughly with those calculated by Kopp's method, but while the latter method gives identical values for isomeric ethers, the molecular volumes calcu-

lated from the coefficient of internal friction were found in all cases to be greater for the normal propyl than for the isopropyl ethers.

G. N. LEWIS.

KURZES REPETITORIUM DER ORGANISCHEN CHEMIE. Für Studierende bearbeitet von DR. KURT DAMMANN. Freiburg in Breisgau: Herdersche Verlagshandlung. 1906. (B. Herder, agent, St. Louis.) 1—xiii+256 pp. Price, \$1.25 net.

As its name implies this book contains condensed statements of the more important facts in organic chemistry. These are arranged, both typographically and as to descriptive matter, in convenient form for students preparing for an examination in the subject. The book does not purport to be a text-book and, consequently, the author contents himself with giving as briefly as possible the general formula, methods of preparation, and characteristic reactions of the different classes of organic compounds. In small print are given details concerning the important members of the various classes. The compilation has been well done. The convenient size and shape of the book, which can be carried in the pocket, the simplicity of its arrangement, and the fact that the material which has been inserted has been selected with discrimination, will make the book of value for the purpose for which it was written.

J. F. NORRIS.

THE CYANIDE PROCESS. By ALFRED S. MILLER. New York: John Wiley and Sons. 1906. Price, \$1.00.

Much has been written describing the cyanide process and its chemistry, yet there would seem to be a place for just such a little treatise as that here presented.

The first two chapters contain a general description of the process and the elements commonly met with in gold and silver ores which interfere with its successful working. Chapter three contains the chemistry of the process, methods of analyses and instructions for the proper control of the process.

Chapter four includes methods for the determination of the applicability of the cyanide process to the treatment of an ore. Chapter five includes suggestions relating more particularly to the practical operation of the process, and the book closes with a chapter briefly describing some of the numerous modifications of the process patented, and otherwise.

The book is well printed and illustrated. The style is simple

and accurate. The writer has, as is indicated in the preface, succeeded in writing a "compact" and "to the point" book.

WM. HOSKINS.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM. By R. J. STRUTT. New York: Longmans, Green & Co.; London: Edward Arnold. 1906. 8vo. Second edition, viii+215 pp.

The new edition differs but slightly from the first, which appeared two years earlier. A number of eliminations and additions have been made in order to bring the book into accord with more recent views; the size of the volume remains unchanged. A few misprints and erroneous or objectionable statements persist from the first edition. Thus, it is stated, p. 29, that thorium has the heaviest atom of any known element. On p. 67, the velocities of the cathode rays as given in the table should be multiplied by  $10^{10}$ . On p. 30 we read "for, if there is any scientific doctrine which is established by experience, it is that the amount of energy in the universe remains strictly the same at all times." This oft-repeated, extravagant substitute for the first law of energetics is neither "scientific" nor "established by experience." It is purely a transcendental, metaphysical dictum. The reviewer's high opinion of the book was fully expressed in the review of the first edition.<sup>1</sup>

HERBERT N. MCCOY.

## RECENT PUBLICATIONS.

A TEXT-BOOK OF SANITARY AND APPLIED CHEMISTRY, OR THE CHEMISTRY OF WATER, AIR AND FOOD. By Edgar H. Summerfield Bailey. New York: Macmillan. 1906. 20+345 pp. \$1.40.

CHEMISTRY OF THE ALBUMENS: TEN LECTURES DELIVERED IN THE PHYSICAL DEPARTMENT OF UNIVERSITY COLLEGE, LONDON. By S. Barnett Schryver. Philadelphia: P. Blakiston's Son & Co. 1906. 5+192 pp. \$2.00.

MODERN SOAPS, CANDLES AND GLYCERIN. PRACTICAL MANUAL OF MODERN METHODS OF UTILIZATION OF FATS AND OILS IN MANUFACTURE OF SOAPS AND CANDLES, AND OF THE RECOVERY OF GLYCERIN. By L. Lloyd Lamborn. London: Lockwood. 1906. 708 pp. 301.

MODERN DAIRY-FARMING. PRACTICAL HANDBOOK ON THE MANAGEMENT OF MILCH COWS AND THE PROFITABLE UTILIZATION OF MILK. By H. L. Puxley. London: U. Gill. 1906. 244 pp. 316.

CATECHISM ON PRODUCER GAS. By S. S. Wyer. London: Spon. 1906. 416.

<sup>1</sup> This Journal, 27, 324 (1905).

REPORT OF PRINCIPAL CHEMIST ON WORK OF GOVERNMENT LABORATORY. London: Wyman. 1906. 13.

LESSONS IN SCIENCE: A PRELIMINARY COURSE OF PHYSICS AND CHEMISTRY. By R. Arman Gregory and Arthur T. Simmons. N. Y.: Macmillan & Co. 1906. 8+399 pp. \$0.90.

AN INTRODUCTION TO CHEMICAL CRYSTALLOGRAPHY: AUTHORIZED TRANSLATION BY HUGH MARSHALL. By P. Groth. New York: John Wiley & Sons. 1906. 7+123 pp. \$1.25.

EXAMINATION OF WATER (CHEMICAL AND BACTERIOLOGICAL). By W Pitt Mason. Third revised edition. New York: John Wiley & Sons. 1906. 6+123 pp. \$1.25.

GIFTVERKAUF-BUCH FÜR APOTHEKER UND DROGISTEN. ... By H. Böttger. Third edition. Berlin: J. Springer. 1906. 40 pp. Marks 3.-

DER CHEMISCHE UNTERRICHT AN DER SCHULE UND DER HOCHSCHULUNTERRICHT FÜR DIE LEHRER DER CHEMIE. By C. Duisberg. Leipzig: O. Spamer. 1906. 48 pp. Marks -.80.

LE COTON: CULTURE, PRÉPARATION, COMMERCE. By A. Lalière. Paris: A. Challamel. 10 francs.

PRINCIPES THÉORIQUES DE MÉTHODES D'ANALYSE MINÉRALE FONDÉES SUR LES RÉACTIONS CHIMIQUES. By G. Chesneau. Paris: H. Dunod et E. Pinat. 244 pp. 4 fr. 50.

LES SUCRES: LE CACAO, LE CAFÉ, LE THÉ, LE CHOCOLAT. By Girard. Paris: J. B. Baillière. 1906. 96 pp. 1 fr. 50.

NOTES ON QUALITATIVE ANALYSIS. CONCISE AND EXPLANATORY. By H. J. H. Fenton. Revised edition. Cambridge: Cambridge University. 1906. 156 pp. 6s.

GALVANIC CELLS PRODUCED BY THE ACTION OF LIGHT. CHEMICAL STATICS AND THE DYNAMICS OF REVERSIBLE AND IRREVERSIBLE SYSTEMS UNDER THE INFLUENCE OF LIGHT. By M. Wilderman. London: Dulau. 1906. 316.

A MANUAL OF QUALITATIVE ANALYSIS AND OF MEDICAL CHEMISTRY FOR PHYSICIANS AND STUDENTS. By C. Platt. Fifth edition. Philadelphia: John Jos. McVey. 1906. 9+243 pp. \$2.00.

METALLURGY OF CAST IRON: A COMPLETE EXPOSITION OF THE PROCESSES INVOLVED IN ITS TREATMENT CHEMICALLY AND PHYSICALLY, FROM THE BLAST FURNACE TO THE TESTING MACHINE. By T. Dyson West. Tenth edition. Cleveland: Cleveland Printing & Publishing Co. 1906. 20+627 pp. \$3.00.

RADIOAKTIVITÄT UND DIE KONSTITUTION DER MATERIE. By F. Himstedt. Freiburg i/B: Speyer & Kaerner. 1906. 31 pp. Marks -.90.

SECHS VORTRÄGE ÜBER DAS THERMODYNAMISCHE POTENTIAL UND SEINE ANWENDUNGEN AUF CHEMISCHE UND PHYSIKALISCHE GLEICHGEWICHTS-PROBLEME. By J. J. van Laar. Braunschweig: F. Vieweg & Sohn. 1906. 8+119 pp. Marks 3.50. (Bound, Marks 4.20.)

PRÉCIS D'ANALYSE CHIMIQUE QUANTITATIVE DES SUBSTANCES MINÉRALES. By C. Friedheim. Paris: Ch. Béranger. 1906. 18 fr.



**THE ANALYSIS AND SOFTENING OF BOILER FEED-WATER.** By Edmund and Fritz Wehrenfennig. Translated by D. W. Patterson. Second edition revised. New York: John Wiley & Sons. 1906. 14+290 pp. \$4.00.

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**SCIENCE YEAR BOOK WITH ASTRONOMICAL, PHYSICAL AND CHEMICAL TABLES. SUMMARIES OF PROGRESS IN SCIENCE, DIRECTORY AND DIARY FOR 1906.** By B. F. S. Baden-Powell. London: Van Nostrand. 1906. 367 pp. \$2.00.

**CANE JUICE DEFECATION.** By W. L. Bass. Translated by S. F. De Valasco. Brooklyn: Van Nostrand. 1905. 206 pp. \$3.00.

**MANUFACTURE OF VARNISHES AND KINDRED INDUSTRIES, BASED ON AND INCLUDING THE "DRYING OILS AND VARNISHES" OF ACH. LIVACHE** By J. G. McIntosh. Second greatly revised English edition. Vol. 1, Oil Crushing, Refining and Boiling, Manufacture of Linoleum. . . London: Van Nostrand. 1904. 153 pp. \$3.50.

**REPORT OF THE COMMITTEE ON STANDARD METHODS OF WATER ANALYSIS TO THE LABORATORY SECTION OF THE AMERICAN PUBLIC HEALTH ASSOCIATION.** Presented at the Havana Meeting, January 9, 1905. Chicago: Van Nostrand. 1905. 141 pp. \$1.25.

**CONDUCTIVITY OF LIQUIDS: METHODS, RESULTS, CHEMICAL APPLICATIONS AND THEORETICAL CONSIDERATIONS.** By O. F. Tower. Easton, Pa.: Van Nostrand. 182 pp. \$1.50.

**MICROSCOPY OF VEGETABLE FOODS WITH SPECIAL REFERENCE TO THE DETECTION OF ADULTERATION AND THE DIAGNOSIS OF MIXTURES.** By A. L. Winton. New York: Van Nostrand. 1906. 701 pp. \$7.50.

**THE NATURE OF ORE DEPOSITS.** By Richard Beck. Translated and revised by Walter Harvey Weed. New York: Van Nostrand. 2 vols. \$8.00.

**PUBLIC WATER SUPPLIES. REQUIREMENTS, RESOURCES AND THE CONSTRUCTION OF WORKS.** By F. E. Turneure. Phila.: Phila. Book Co. 14+746 pp. \$5.00.

**SMOKELESS POWDER. NITRO-CELLULOSE, AND THEORY OF THE CELLULOSE MOLECULE.** By John B. Bernadou. Phila.: Phila. Book Co. 8+200 pp. \$2.50.

**CAST IRON. A RECORD OF ORIGINAL RESEARCH.** By William J. Keep. Phila.: Phila. Book Co. 13+225 pp. \$2.50.

CRYSTALLIZATION OF IRON AND STEEL. By J. W. Mellor. New York: J. Wiley & Sons. 1906. \$1.60.

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GARBAGE CREMATORIES IN AMERICA. By William Mayo Venable. New York: J. Wiley & Sons. 1906. 10+200 pp. \$2.00.

TECHNOLOGY OF PAINT AND VARNISH. By Alvah H. Sabin. New York: J. Wiley & Sons. 1906. \$3.00.

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ELEMENTARY CHEMISTRY. PROGRESSIVE LESSONS IN EXPERIMENT AND THEORY. By F. R. L. Wilson and G. W. Hedley. Part 2. London: Frowde. 1906. 402 pp. 51.

GENERAL PRINCIPLES OF ORGANIC SYNTHESSES. By Petr Petrovich Aleksieev. Authorized translation with revision and additions, by J. Merritt Matthews. New York: J. Wiley & Sons. 1906. 246 pp. \$3.00.

# THE JOURNAL

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## ON THE ELEMENTARY NATURE AND ATOMIC WEIGHT OF TELLURIUM.

BY JAMES F. NORRIS.

SOME years ago Norris, Fay and Edgerly<sup>1</sup> undertook a study of the elementary nature of tellurium in order to discover,<sup>1</sup> if possible, the cause of the anomalous relation of the element to the periodic law. Up to the time of the publication of the work reported by them, no systematic study of this problem had been described. A number of investigators had determined the atomic weight of tellurium, after what appeared to be a careful purification of the compounds to be analyzed. The methods of purification used, however, were not of such a nature as to be relied upon to free the compounds investigated from undiscovered elements. With this fact in mind an investigation was undertaken. Since the work was started, great activity has been shown in this field, and a number of papers have appeared on the atomic weight of tellurium. The most noteworthy is that of Köthner,<sup>2</sup> to which the reader is referred for a full historical account of the subject.

The work about to be described was inspired by a statement in the Faraday memorial lecture delivered by Mendeléeff in 1889. In discussing the periodic law Mendeléeff recounts the great service which the law has rendered in bringing about the correction of a number of atomic weights. In seeking to explain the

<sup>1</sup> Am. Ch. J. 23, 105.

<sup>2</sup> Ann. 319, 1.

high value of the atomic weight of tellurium, he expresses the opinion that the so-called element consists of two elements: one, true tellurium with an atomic weight of approximately 125, and the other, an element with a higher atomic weight, which would find a place in the periodic classification in the vacant space under tellurium. To this undiscovered element Mendeléeff gives the name *divitellurium*. He sketches the chemical and physical properties of such an element as he had already done so successfully in other cases.

It was to test this hypothesis that the work which has been published and that described below were undertaken. In order to make the study of the problem complete, it seemed necessary to endeavor to discover first, whether an undiscovered element, which did not belong to the sulphur group, was present in tellurium, and second, whether the hypothesis of Mendeléeff could be given any experimental basis.

In seeking a solution of the first problem, a sample of tellurium, which had been freed from all known elements, was converted into a compound of the formula  $\text{Na}_2\text{S}_4\text{TeO}_6$ . This substance is a derivative of sodium pentathionate in which one sulphur atom has been replaced by one of tellurium. From this compound the tellurium was recovered by means of a reaction which is characteristic of pentathionates. Determinations of the atomic weight of the tellurium, which had been purified in this way, gave as a mean from several experiments the value 127.46.<sup>1</sup> This number was identical with that obtained with a sample of the element which had not been subjected to this particular method of treatment. As it is improbable that an element not in the sulphur group would show the power to replace, in part, sulphur in such a characteristic compound as sodium pentathionate, the conclusion can be drawn that tellurium contains no element which does not show the characteristic reactions of the sulphur group.

In order to test experimentally the hypothesis of Mendeléeff, carefully purified compounds of tellurium were subjected to fractionation. In the paper already published an account is given of the study of the products resulting from a fractional

<sup>1</sup> For the atomic weights used in the calculation see p. 1683. If no vacuum correction is made and 14.04 is taken as the atomic weight of nitrogen this value becomes 127.62.

crystallization of the double bromide of tellurium and potassium. Atomic weight determinations of the element obtained from these products agreed with one another within the limits of accuracy of the method used. Notwithstanding this result the work was continued, as it was thought that the breaking down of the salt by crystallization might not have been effected on account of the fact that its constituents were isomorphous with each other. The method described below, which was finally selected to test the question, involved the study of the products resulting from the fractional distillation of tellurium dioxide.

Other investigators have used compounds which have been distilled. Brauner used sublimed tellurium tetrabromide in one of his atomic weight determinations. As the difference between the boiling-points of the bromides of selenium and tellurium is not great, it is evident that a long-continued process of fractionation would be necessary to free tellurium bromide from the analogous compound of ditellurium. Since this work was started, Köthner has determined the atomic weight of distilled tellurium. The difference between the boiling-points of selenium and tellurium is such that it would be reasonable to expect that another element in the same family with a higher atomic weight would have a boiling-point not far from that of tellurium. It appeared from the above-mentioned facts that it was worth while to re-study the problem, if a better method could be found. The properties of the oxides of sulphur, selenium and tellurium are such, that it seemed that a study of tellurium dioxide would give results which would furnish a definite answer to the question as to the elementary nature of tellurium. Sulphur dioxide boils at  $-8^{\circ}$ , selenium dioxide is volatile at  $200-250^{\circ}$ , and tellurium dioxide is converted into vapor slowly at a bright red heat. In the light of these facts it is highly probable that the oxide of another element in the same family, with a higher atomic weight, would be very much less volatile than is tellurium dioxide, if volatile at all at the temperature of the Bunsen flame.

The oxide investigated was prepared from a sample of nitrate which had been carefully purified. The source of the material and the methods of preparation and purification used are described in detail in the paper cited above. In the distillation of the oxide the process was stopped after about three-quarters of

the product had been volatilized. The part which had distilled was redistilled, until as before three-quarters of it was collected. This process of fractionation was repeated five times. The oxide was distilled from platinum at the highest temperature obtainable with a Bunsen burner; under these conditions the oxide was collected at the rate of about 0.15 gram per hour.

The atomic weights were determined of the tellurium in the first residue, which should have contained the less volatile oxide, and of the tellurium in the oxide which had been sublimed five times. As a standard for comparison the atomic weight of the tellurium in a sample of oxide which had not been sublimed was determined. The method of determining the atomic weight which was used was that first described in the paper by Norris, Fay and Edgerly already cited, namely, the conversion of the nitrate into the oxide. This method has recently been used with success by Köthner.

The results were as follows: The average atomic weight obtained in the case of the tellurium from the undistilled oxide was 127.50. The average of three determinations of the value, when the oxide which had been distilled five times was used, was also 127.50. The original residue from the first fractionation gave the atomic weight 127.46. It is evident from these results that the fractional distillation effected no decomposition in the tellurium dioxide. The mean of all the values for the atomic weight, agrees well with the most trustworthy determinations which have been published, when these are calculated on the same basis.

The results seem to the writer to furnish positive evidence in favor of the elementary nature of tellurium. With a difference of about  $250^{\circ}$  between the boiling-points of sulphur dioxide and selenium dioxide, and a difference of  $500^{\circ}$  to  $600^{\circ}$  between the same constants for selenium dioxide and tellurium dioxide, it is evident, from all analogies in the properties of compounds of members of the natural families in the periodic classification, that the oxide of an element which should find its place in the formulation of the law in the vacant space under tellurium, should be very much less volatile than tellurium dioxide. Its separation by the process used should have been at least in part effected. Even if tellurium contains an element which does not belong to the sulphur family, the possibility of its oxide having the same

volatility as that of tellurium dioxide is very remote. As there was no evidence of even the slightest change in the properties of the compound, or in the atomic weight as a result of the tests applied, and as these tests seem to be reliable and well suited to answering the question, the conclusion can be drawn that the statement that tellurium is an element rests upon a firmer experimental basis than heretofore.

#### EXPERIMENTAL.

The source and preliminary purification of the material used in this investigation are described at length in the paper already cited. A sample of the basic nitrate of tellurium which had been recrystallized three times from nitric acid was made use of in the work. From this the oxide was prepared by heating at increasing temperatures until all nitric acid had been removed.

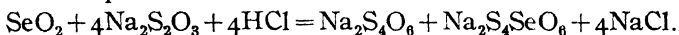
About 25 grams of the oxide were fractionally distilled. The point at which tellurium dioxide volatilizes is so high it could not be distilled in a tube in the usual way. After tests of a number of methods that selected was as follows: The oxide was heated to bright redness in a platinum crucible, over which was placed a funnel with the stem bent at right angles. To this last was attached a glass tube provided with a cork and an exit tube, the open end of which was covered with filter-paper. A rapid stream of air was drawn through the tube and funnel. The tellurium dioxide which had been vaporized was swept through the funnel and was collected as a fine powder which settled in the tube and on the paper which covered the exit from the tube. When the crucible which contained the oxide was heated to bright redness, between 0.1 and 0.2 gram of the oxide distilled in one hour.

The distillation was started with about 25 grams of tellurium dioxide. This was heated until a residue of 7 grams remained. The 18 grams which had been vaporized were again distilled until there was a residue of about 3 grams. The twice distilled oxide was redistilled until about 12.5 grams had been collected. The process was repeated and 8 grams were distilled off. In the fifth distillation the oxide which was collected weighed about 6 grams.<sup>1</sup> The fractions of the oxide resulting from the distilla-

<sup>1</sup> The author gladly acknowledges his indebtedness to Mr. C. F. Swan, of the Massachusetts Institute of Technology, who carried out the fractioning of the oxide, which was a tedious process, requiring a very long time for its completion.

tion, were converted into the basic nitrate, recrystallized twice from nitric acid, and finally purified for analysis as described below.

In endeavoring to test the question whether tellurium contains an unknown element which does not belong to the sulphur group, another method of purification was made use of. Facts which were reported by Norris and Fay in their papers on the volumetric estimation of selenium and tellurium suggested a convenient way of attacking this problem. It was shown that a reaction represented by the following equation takes place when selenium dioxide, sodium thiosulphate and hydrochloric acid are brought together in aqueous solution:



The selenopentathionate is very unstable and cannot be obtained from solution. That the salt was present was shown by the fact that the solution exhibited all the reactions which are characteristic of pentathionates. Sodium pentathionate is stable in an acid solution, but is instantly decomposed when brought into contact with alkalis, being converted into sodium tetrathionate and free sulphur. The analogous selenium compound suffered decomposition in the same way and was converted into the tetrathionate and selenium.

It was also shown that similar reactions take place when the product of the reaction between tellurium dioxide, sodium thiosulphate and hydrochloric acid is treated with alkalis. A sample of pure tellurium dioxide was converted into the pentathionate derivative which was then treated with sodium hydroxide. It seemed highly probable that the precipitated tellurium so obtained was free from any element which did not have the power to replace sulphur in a pentathionate. The precipitate was treated with hydrochloric acid to free it from any hydroxide that may have been thrown down by the alkali.

In order to carry out the reaction successfully the substances are brought together in the quantities required by the chemical equation, with the exception that more hydrochloric acid than is called for must be used in order to keep the tellurium dioxide in solution. The solution must be dilute and cold in order to prevent decomposition of the sodium thiosulphate by the excess of acid. Addition of a small quantity of alkali to the acid solution causes the precipitation of a part of the tellurium present.



This precipitation continues until the solution is rendered alkaline. The tellurium obtained in the way outlined above was converted into the basic nitrate, which was crystallized twice and finally prepared for analysis.

In the final purification of the nitrate it was crystallized from dilute nitric acid (sp. gr. 1.25), which was prepared from purified materials. The water used for dilution was twice distilled, the last time from alkaline permanganate. The nitric acid used was a good sample of chemically pure acid, which was redistilled slowly from a platinum still, provided with a platinum condenser and receiver. The diluted acid was kept in bottles which had been repeatedly treated with warm nitric acid. The salt was crystallized in porcelain dishes which had been carefully cleaned with hot acid. Saturated solutions of the salt were evaporated at about 85° until reduced to about one-fourth their original bulk. The hot mother-liquor was immediately removed and the crystals were washed with redistilled concentrated nitric acid. The crystals were again dissolved in the purified acid and re-crystallized.

It was found necessary, in order to obtain concordant results, to use, in determining the ratio between the weights of nitrate and oxide, only crystals which had been formed during the evaporation. In every case where the mixture of crystals and mother-liquor was allowed to stand over night before the crystals were removed, low values of the atomic weight, which varied with different samples, were obtained. It was evident that spontaneous evaporation caused the formation of crystals which contained mother-liquor.

The crystals which were removed from the hot solution were washed a number of times with redistilled concentrated nitric acid and were then ground to a very fine powder in an agate mortar, while still moist with acid. The finely ground nitrate was transferred by means of a platinum spatula to a well-cleaned porous tile, which immediately removed most of the acid clinging to the powder. The tile, with the nitrate which had been placed on it in a small pile, was placed in a desiccator which contained concentrated sulphuric acid and solid potassium hydroxide. The air was exhausted from the desiccator, which was left undisturbed for a day. The nitrate was then removed from the tile, care being taken to reject the portion which had come in

contact with the tile. The product, which was at this stage in the form of a hard lump, was readily reduced to a fine powder by breaking it with a few strokes of a spatula. The nitrate was next kept for at least three days in a vacuum over phosphorus pentoxide.

This method of removing the excess of acid liquid from the nitrate is an improvement over that used by Köthner in his work. Köthner was of the opinion that as the acid was removed by evaporation from the crystals, they were partially decomposed to the oxide with loss of acid. This may have been the case when the acid was removed at an elevated temperature as Köthner did it. In order to prevent this decomposition he washed the crystals with mixtures of nitric acid and alcohol, using successively a larger proportion of alcohol in the mixture, until pure alcohol was used. This method is tedious and great precautions are necessary. In the preliminary work a number of samples were prepared by Köthner's method. These gave the same results as samples prepared as described above.

In determining the ratio between the weights of the nitrate and oxide, the usual precautions necessary for accurate results were taken. The weights were calibrated and a balance sensitive to 0.03 mg. was used. The weighings were made by substitution after the crucibles had stood in the balance case at least two hours. A crucible like those used to contain the nitrate was used as a tare.

The samples of nitrate were heated in platinum crucibles to constant weight at 140° in a current of air dried by passing over phosphorus pentoxide. This first heating of the salt, which brought it to constant weight, was continued for four hours. The samples were weighed before and after this heating at 140°. In no case was the loss in weight as a result of heating for four hours greater than 0.1 mg. The decomposition of the nitrate was brought about slowly in order to avoid the loss of tellurium dioxide by mechanical removal along with gases evolved. The crucibles were heated about six hours at 250°, six hours at 300°, three hours at 350°, three hours at 400–450°. The crucibles, resting on pieces of platinum foil inside a large covered porcelain crucible, were next heated for four hours at the highest temperature procurable with a Bunsen burner. The oxide formed from the nitrate in this way was finally fused by the application

of a free flame for a few seconds. A test showed that the oxide contained no nitric acid and the glassy condition produced by the fusion precluded the possibility of any enclosed gases.

The results of the analyses follow:

No.	Weight $2\text{TeO}_2 \cdot \text{HNO}_3$	Weight $\text{TeO}_2$	Atomic weight.
1.....	2.28215	1.90578	127.47
2.....	2.35429	1.96615	127.53
3.....	1.86853	1.56042	127.49
4.....	1.77348	1.48110	127.49
5.....	2.31048	1.92938	127.44
6.....	2.14267	1.78936	127.50
7.....	2.35523	1.96676	127.45
8.....	2.18860	1.82780	127.54
9.....	3.29158	2.74881	127.50
10.....	2.27516	1.89993	127.46
11.....	2.53164	2.11410	127.46
12.....	2.01327	1.68121	127.45

Average, 127.48

In the second and third columns are given the apparent weights of the nitrate and oxide. In calculating the values of the atomic weight, a vacuum correction was made of +0.150 mg. for each gram of nitrate and +0.066 mg. for each gram of oxide. The specific gravity of tellurium dioxide has been reported as 5.76. The value of this constant for the basic nitrate of tellurium was found to be 4.26 at  $22^\circ/4^\circ$ . The atomic weights used in the calculation were H, 1.0076; N, 14.01; O, 16.

When the results are calculated in the manner used by Köthner, namely, H, 1.01; N, 14.04; O, 16 and no vacuum corrections are applied, the average is 127.64. Köthner's average was 127.63.

The results given under numbers 1, 2 and 3, were those obtained with a sample of nitrate which had been purified by crystallization only. In the paper by Norris, Fay, and Edgerly it was stated that crystallization of the basic nitrate served to purify it from all other metals. These results confirm that statement. Köthner showed by a spectroscopic examination that the nitrate prepared by him contained silver and gold. When he determined the atomic weight of tellurium, using a sample of nitrate made from the metal which had not been distilled, he obtained as the atomic weight, the value 127.36, which differed by 0.27 unit from the value found when distilled tellurium was used. He considered the cause of this difference to be the presence of

silver and gold in the nitrate which was prepared from undistilled tellurium. The results given above, which were obtained with a sample of nitrate which had been purified by crystallization alone, are practically identical with those obtained from a sample of nitrate prepared from the oxide which had been five times distilled.

The results obtained with the nitrate prepared from the tellurium which had been converted into the telluropentathionate are recorded in experiments numbered 4, 5 and 6. In the experiment numbered 7 the nitrate used was prepared from a sample of oxide which had been distilled but once, while in experiments 8 and 9 the oxide from which the nitrate was made had been distilled five times. In numbers 10, 11 and 12 are recorded the results of the analyses of samples of nitrate prepared from the residue from the first distillation. If the divitellurium of Mendeléeff had been present, the atomic weight of this fraction should have been much higher than 127.48.

The results show clearly that the application of the methods studied effected no decomposition of tellurium. As these methods would have shown the presence of an unknown element with the properties which have been assigned to divitellurium by Mendeléeff, the conclusion can be drawn that no such element is present. The work adds to the experimental evidence in favor of the elementary nature of tellurium.

The atomic weight found agrees well with the most reliable values, which have been determined by others.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## THE CARRYING DOWN OF AMMONIUM OXALATE BY OXALATES OF THE RARE EARTHS.

BY GREGORY PAUL BAXTER AND ROGER CASTLE GRIFFIN.

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A RAPID and convenient method for approximate atomic weight determinations of the trivalent metals of the rare earths is the "permanganate" method, in which the ratio  $M_2O_3:3C_2O_3$  is determined. In this process a known weight of the oxalate of the rare earth is ignited to oxide and the latter is weighed. Then

a known weight of the same sample of oxalate is dissolved in sulphuric acid and the oxalic acid is titrated with standard potassium permanganate. By dividing the ratio  $\frac{M_2O_3}{M_2(C_2O_4)_3}$  found in the first process by the ratio  $\frac{3C_2O_3}{M_2(C_2O_4)_3}$  found in the second, the ratio  $\frac{M_2O_3}{3C_2O_3}$  is determined, from which the atomic weight may be calculated.<sup>1</sup>

It has already been pointed out by Gibbs<sup>2</sup> and others that the oxalates of the rare earths contain varying amounts of water, and that it is very necessary to grind thoroughly the whole specimen of oxalate which is to be used for analytical purposes, in order to ensure homogeneity of material. Furthermore, the fact has long been recognized that in the presence of potassium or sodium oxalates some of these substances may be carried down by the insoluble oxalates. Large discrepancies in the observed atomic weight as determined by the above method, with material which had been precipitated by oxalic acid or ammonium oxalate, led to the following research upon the effect of varying conditions upon the composition of the oxalates of certain of the rare earths. It is found that ammonium oxalate also, but not oxalic acid, may be carried down in considerable quantities by the rare earth oxalates.

Neodymium was the first element studied. A specimen of oxalate was ignited to oxide and dissolved in a considerable excess of nitric acid. The absorption spectrum of the solution showed the bands of neodymium only. A portion of the solution was then slowly added, with constant stirring, to a solution of a large excess of oxalic acid. The resulting oxalate was washed ten times by decantation with hot water and collected on a porcelain Gooch crucible, provided with a disk of filter-paper instead of asbestos. On testing the filtrate the precipitation of the neodymium was found to be complete. After the oxalate had been dried in an electric air-bath at 120–130° for about twenty hours, it was thoroughly mixed by grinding in a porcelain mortar.

<sup>1</sup> This method was first proposed by Stolba: Sitzber. böhm. Ges., Dec. 1878; Also Chem. News, 41, 31 (1880).

<sup>2</sup> Pr. Am. Acad. 28, 262 (1893).

Portions of about 0.5 gram were then transferred from a weighing-bottle to weighed platinum crucibles, and the crucibles were ignited, first in a Bunsen flame, and finally for several minutes with a blast-lamp. The crucibles were allowed to cool in desiccators and were again weighed. In each case a repetition of the ignition failed to change the weight of the oxide.

Next, portions of from 0.2 to 0.3 of a gram of the oxalate were weighed into Erlenmeyer flasks, and after the addition of about 5 cc. of concentrated sulphuric acid diluted with fifty of water, the flasks were heated on the steam-bath until the oxalate was completely dissolved. Then the oxalic acid was determined by titration with potassium permanganate solution. This solution was standardized with oxalic acid which had been allowed to come to constancy over sulphuric acid of the sp. gr. 1.35. The oxalic acid had been many times recrystallized, first from hydrochloric acid solution, then from pure water until free from chlorides.

Since the weight of oxalate found experimentally was considerably less than 100 per cent., as a check on the process the water content was determined by igniting weighed portions of the oxalate in a porcelain boat in a current of dry air, and absorbing the water in a weighed phosphorus pentoxide tube.

The results of the complete analysis are as follows:

	I.	II.	III.	Average.
Weight of oxalate.....	0.6505	0.5938	0.5865	
Weight of $\text{Nd}_2\text{O}_3$ .....	0.3182	0.2908	0.2869	
Per cent. of $\text{Nd}_2\text{O}_3$ .....	48.92	48.97	48.92	48.94
Weight of oxalate.....	0.3164	0.3230	0.2613	
Vol. of $\text{KMnO}_4$ sol.....	28.03	28.60	23.16	
1 cc. $\text{KMnO}_4 = 0.003547$ gram $\text{C}_2\text{O}_3$ .				
$\text{C}_2\text{O}_3$ calculated.....	0.0994	0.1014	0.0822	
Per cent. of $\text{C}_2\text{O}_3$ .....	31.43	31.41	31.44	31.43
Weight of oxalate.....	0.6575	0.6264		
Weight of water.....	0.1278	0.1241		
Per cent. of water.....	19.44	19.81		19.62
				Total, 99.99

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{48.94}{31.43} = 1.5571$$

$$\text{M} = 144.2 \quad (\text{Nd} = 143.6)$$

The observed value for the atomic weight of neodymium is so near the most probable value of this constant as the purity of the

sample would lead one to expect. Since the oxalate used in the above experiments was precipitated with a very large excess of oxalic acid, the possibility existed that some of the precipitant had been carried down by the precipitate. In order to determine whether this was the case, another sample of the same material was precipitated in a similar manner, but with a very slight excess of oxalic acid.

	I.	II.	III.	Average
Per cent. of $\text{Nd}_2\text{O}_3$ .....	58.02	57.98	57.94	57.98
Per cent. of $\text{C}_2\text{O}_3$ .....	37.25	37.27	37.17	37.23
Ratio $\text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{57.98}{37.23} = 1.5573$ .				
$\text{M} = 144.2 \quad (\text{Nd} = 143.6)$				

The agreement of the values for the atomic weight of neodymium obtained from the analyses of oxalate which had been precipitated with a very large and with a slight excess of oxalic acid shows conclusively that no appreciable tendency for the carrying down of oxalic acid exists.

Precipitation by means of ammonium oxalate was next investigated. A solution of neodymium oxide in nitric acid was nearly neutralized with ammonia, and was added to a slightly ammoniacal solution of a small excess of ammonium oxalate. Precipitation was found to be complete. After the precipitation the supernatant liquid was faintly acid. By adding the neodymium solution to the oxalate, occlusion, if it exists at all, is to be expected to be at a maximum. The oxalate was thoroughly washed, dried and powdered. Then it was analyzed as before.

	I.	II.	III.	Average.
Per cent. of $\text{Nd}_2\text{O}_3$ .....	50.65	50.58	50.70	50.64
Per cent. of $\text{C}_2\text{O}_3$ .....	37.99	38.01	38.02	38.01
Per cent. of $\text{H}_2\text{O}$ .....	11.28	11.22		11.25
				Total, 99.90

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{50.64}{38.01} = 1.3322$$

$$\text{M} = 119.9 \quad (\text{Nd} = 143.6)$$

Since it was certain from these results that the salt contained too much oxalate, and since it was probable that the excess was due to ammonium oxalate which had been carried down by the neodymium oxalate, a portion of the precipitate was tested for ammonia, after solution in nitric acid, by adding an excess of potassium hydroxide. Ammonia was evolved in quantity. It

was evident, therefore, that ammonium oxalate is carried down by neodymium oxalate to a considerable extent. The determination of the water in this oxalate includes the ammonia as well as the water. However, since ammonium oxalate, when heated, breaks up partially into cyanogen and water, this determination is slightly in error. During the analysis of the oxalate for water the odor of cyanogen was perceptible.

Neodymium oxalate, which had been precipitated by addition to a nearly saturated solution of ammonium oxalate, was found to contain a still larger proportion of ammonium oxalate.

	I.	II.	III.	Average.
Per cent. of $\text{Nd}_2\text{O}_3$ .....	49.56	49.70	49.59	49.62
Per cent. of $\text{C}_2\text{O}_3$ .....	39.63	39.66	39.66	39.65
Per cent of $\text{H}_2\text{O} + \text{NH}_3$ .....	9.91	10.31		10.11

Total, 99.38

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{49.62}{39.65} = 1.2514$$

$$\text{M} = 111.2 \quad (\text{Nd} = 143.6)$$

Upon the assumption that the average atomic weight of the metals in this sample is 144.2, the amount of  $\text{C}_2\text{O}_3$  corresponding to 49.62 per cent. of oxide is 31.86. The difference between this proportion and that observed is 7.79, which in turn corresponds to 3.68 per cent. of ammonia. In order to determine whether this proportion of ammonia actually existed in the oxalate, the latter was analyzed for ammonia. Weighed portions of the oxalate were dissolved in dilute sulphuric acid and the solutions were diluted to about one-half liter. Then they were transferred to a liter retort, into the tubulature of which was fitted a dropping funnel containing a strong solution of ammonia-free potassium hydroxide. The potassium hydroxide was slowly added to the solution in the retort and the ammonia set free was distilled into standard hydrochloric acid in the usual way. Blank tests were made and slight corrections were applied. The percentage of ammonia obtained experimentally agrees very closely with that calculated above.

	I.	II.	III.	IV.	Average.
Weight of oxalate.....	0.4343	0.2872	0.3290	0.3098	
cc. $\text{N}/_{10}$ HCl used.....	9.22	6.10	6.76	6.46	
Per cent. of ammonia.....	3.61	3.62	3.55	3.55	3.58
				Calculated,	3.68

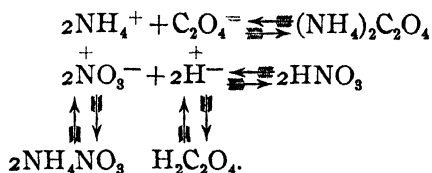
Next, precipitation in neutral solution with ammonium oxalate



was investigated. A solution of neodymium chloride as nearly neutral as possible was prepared by evaporating to dryness on the steam-bath a solution of the oxide in hydrochloric acid, and repeating the evaporation several times after dissolving the residue in water. This solution was added drop by drop with continual agitation to a concentrated hot solution of ammonium oxalate. Occlusion is to be expected to the same extent here as in the previous case. Such proved to be the result.

	I.	II.	III.	Average.
Per cent. of $\text{Nd}_2\text{O}_3$ .....	49.57	49.49		49.53
Per cent. of $\text{C}_2\text{O}_3$ .....	39.25	39.24	39.25	39.25
Per cent. of $\text{H}_2\text{O} + \text{NH}_3$ .....	11.28	11.74		11.51
			Total,	100.29
Per cent. of $\text{NH}_3$ .....	3.50	3.50		3.50
Per cent. of $\text{C}_2\text{O}_3$ corresponding to $\text{NH}_3$ .....				37.41
Per cent. of $\text{C}_2\text{O}_3$ corresponding to $\text{Nd}_2\text{O}_3$ .....				31.84
Ratio $\text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 =$	$\frac{49.53}{31.84}$			1.5555
M = 144.0	Theoretical = 144.2			

It has been pointed out by Richards that occlusion of any substance is proportional to the concentration of that substance in the molecular condition at the moment of precipitation.<sup>1</sup> In the present instance, since ammonium oxalate is the substance occluded, occlusion should increase with increasing concentration of molecular ammonium oxalate at the moment of precipitation. This has already been found to be the case when precipitation is carried out in neutral or very nearly neutral solution. In a solution containing much strong acid, however, the concentration of molecular ammonium oxalate would be very low, for the reaction between the hydrogen ion and the oxalate ion is nearly complete, even when the hydrogen ion concentration is not large. In the case of nitric acid the equilibrium with ammonium oxalate may be represented as follows:



If then neodymium oxalate is precipitated by ammonium

<sup>1</sup> Pr. Am. Acad. 35, 377; 36, 377.

oxalate in the presence of much nitric acid, little or no carrying down of ammonium oxalate is to be expected.

In the next experiment neodymium nitrate was added to a hot, nearly saturated solution of ammonium oxalate containing a large amount of nitric acid. The precipitate was washed with hot water, dried, powdered and analyzed as before. The analysis of the precipitate confirms the prediction made above. The precipitate contained a mere trace of ammonia, which may account for the slight difference between the observed and theoretical results.

	I.	II.	Average.
Per cent. of $\text{Nd}_2\text{O}_3$ .....	52.73	52.73	52.73
Per cent. of $\text{C}_2\text{O}_3$ .....	33.90	33.91	33.91
Per cent. of $\text{H}_2\text{O}$ .....	12.39	12.53	12.46

Total, 99.10

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{52.73}{33.91} = 1.5551$$

$$\text{M} = 144.0 \quad \text{Theoretical} = 144.2$$

Praseodymium oxalate also was studied in the same way. To a solution of praseodymium nitrate containing nitric acid, an excess of oxalic acid solution was added, drop by drop, with continual agitation. The oxalate was thoroughly washed with water, dried in an air-bath, powdered in a mortar and analyzed as in the case of neodymium. The oxalate, upon ignition, was eventually converted into a black oxide, of the composition  $\text{Pr}_4\text{O}_7$ .<sup>1</sup>

	I.	II.	III.	IV.	Average.
Ratio $\text{Pr}_4\text{O}_7$ : oxalate.....	58.50	58.56			58.53
Per cent. of $\text{Pr}_2\text{O}_3$ .....	57.12	57.17			57.15
Per cent. of $\text{C}_2\text{O}_3$ .....	37.41	37.24	37.17	37.23	37.26
Per cent. of $\text{H}_2\text{O}$ .....	6.42	6.23			6.33

Total, 100.74

$$\text{Ratio } \text{Pr}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{57.15}{37.26} = 1.5338$$

$$\text{Pr} = 141.7 \quad \text{Theoretical} = 140.5$$

The difference between the experimental and theoretical values for the atomic weight of praseodymium may be due to uncertainty either as to the purity of the material employed or as to the composition of the oxide formed by ignition of the oxalate.

A solution of the same praseodymium material containing only a very slight excess of nitric acid, was then precipitated by

<sup>1</sup> Dammer: Handb. der anorg. Chem. 3, 42.

addition to a hot concentrated slightly ammoniacal solution of ammonium oxalate. Precipitation was complete. The precipitate contained very nearly as much ammonia as neodymium oxalate when precipitated under the same conditions.

	I.	II.	III.	Average.
Ratio $\text{Pr}_4\text{O}_7$ : oxalate .....	50.48	50.53		50.51
Per cent. of $\text{Pr}_2\text{O}_3$ .....	49.28	49.33		49.31
Per cent. of $\text{C}_2\text{O}_3$ .....	38.98	39.01		39.00
Per cent. of $\text{NH}_3$ .....	3.45	3.40	3.45	3.43
Per cent. of $\text{C}_2\text{O}_3$ corresponding to 3.43 per cent. of $\text{NH}_3$ ..				7.27
Per cent. of $\text{C}_2\text{O}_3$ corresponding to $\text{Pr}_2\text{O}_3$ .....				31.73

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{49.31}{31.73} = 1.5541$$

$$\text{M} = 143.8 \quad \text{Theoretical} = 140.5$$

The yttrium material employed proved to be far from pure, the atomic weight determined with the precipitate from acid solution being 102.9, while the atomic weight of yttrium is 89.0. Yttrium oxalate was precipitated by adding a solution of a slight excess of oxalic acid to an acid solution of the nitrate, and by adding a nearly neutral solution of the nitrate to a large excess of ammonium oxalate. The precipitate formed in the latter fashion proved to contain considerable ammonia, but when a correction is applied for this ammonia, both precipitates yield nearly the same result for the atomic weight of the sample.

## ACID PRECIPITATION.

	I.	II.	Average
Per cent. of $\text{Y}_2\text{O}_3$ .....	46.24	46.31	46.28
Per cent. of $\text{C}_2\text{O}_3$ .....	39.37	39.39	39.38
Per cent. of $\text{H}_2\text{O}$ .....	14.48	14.64	14.56

Total, 100.22

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{46.28}{39.38} = 1.1750$$

$$\text{M} = 102.9$$

## NEUTRAL PRECIPITATION WITH AMMONIUM OXALATE.

	I.	II.	Average.
Per cent. of $\text{Y}_2\text{O}_3$ .....	41.22	41.25	41.24
Per cent. of $\text{C}_2\text{O}_3$ .....	44.84	44.97	44.91
Per cent. of $\text{NH}_3$ .....	4.54	4.53	4.53
Per cent. of $\text{C}_2\text{O}_3$ corresponding to 6.95 per cent. of $\text{NH}_3$ ..			9.59
Per cent. of $\text{C}_2\text{O}_3$ corresponding to $\text{Y}_2\text{O}_3$ .....			35.32

$$\text{Ratio } \text{M}_2\text{O}_3 : 3\text{C}_2\text{O}_3 = \frac{41.24}{35.32} = 1.1674$$

$$\text{M} = 102.1$$

The last material investigated was separated from a solution of the rare earths contained in Texas gadolinite by means of fractional precipitation with magnesium oxide. The spectro-scope showed it to be rich in erbium, and to contain samarium, while didymium was entirely absent. A portion of the oxalates was soluble in an excess of ammonium oxalate in neutral solution, although in acid solution precipitation was complete, hence undoubtedly ytterbium was present. In order to make certain that the same material was treated both in neutral solution and in acid solution, precipitation with ammonium oxalate in neutral solution was carried out first, and then, after the precipitate had been analyzed, the same material was dissolved and precipitated with oxalic acid in the presence of considerable nitric acid.

## ACID PRECIPITATION.

	I.	II.	III.	Average.
Per cent. of $M_2O_3$ .....	54.64	54.63	54.63	54.63
Per cent. of $C_2O_3$ .....	34.94	34.94	34.96	34.95

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{54.63}{34.95} = 1.5633$$

$$M = 144.9$$

## NEUTRAL PRECIPITATION WITH AMMONIUM OXALATE.

	I.	II.	Average.
Per cent. of $M_2O_3$ .....	47.88	47.80	47.84
Per cent. of $C_2O_3$ .....	40.05	40.04	40.05

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{47.84}{40.05} = 1.1945$$

$$M = 105.0$$

$$\text{Per cent. of } NH_3 \text{ (calculated. } M = 144.9). \quad 4.47$$

It is interesting to compute the relation of the number of molecules of the oxalates of the rare earths and of ammonia in the precipitates in which the ammonium oxalate content was at a maximum.

	Per cent. of oxide.	Per cent. of ammonia.	Per cent. of ( $NH_4$ ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	Molecules of ( $NH_4$ ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> for one molecule $M_2(C_2O_4)_3$ .
Nd <sub>2</sub> O <sub>3</sub> .....	49.62	3.58	13.05	0.71
Pr <sub>2</sub> O <sub>3</sub> .....	49.31	3.43	12.50	0.68
Y <sub>2</sub> O <sub>3</sub> .....	41.24	4.53	16.51	0.82
Er <sub>2</sub> O <sub>3</sub> (?).....	47.84	4.47	16.29	0.93

The extent of the carrying down of ammonium oxalate by the rare earth oxalates which were investigated is much larger than in other cases of occlusion,<sup>1</sup> and leads to the conclusion that the

<sup>1</sup> Richards: Loc. cit.; Baxter: Am. Ch. J. 28, 298 (1902).

real cause of the phenomenon is not the formation of solid solutions of ammonium oxalate in the rare earth oxalates, as is the case with true occlusion, but the formation of a somewhat unstable double salt, possibly of the general formula  $M_2(C_2O_4)_3(NH_4)_2C_2O_4$ , analogous to the double salts with potassium and sodium oxalates. In either case the extent of the carrying down of ammonium oxalate by the insoluble oxalates would vary with the concentration of the molecular ammonium oxalate at the moment of precipitation.

#### SUMMARY.

(1) The results of the foregoing investigation show that the insoluble oxalates of neodymium, praseodymium, yttrium and certain other of the rare earths, exhibit a strong tendency to carry down ammonium oxalate, when precipitation takes place in neutral or nearly neutral solution.

(2) In the case of neodymium, it is shown that the amount of ammonium oxalate carried down is dependent upon the concentration of molecular ammonium oxalate at the moment of precipitation.

(3) Furthermore, it is shown that neodymium oxalate has no tendency to carry down oxalic acid, and that the occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of ammonium oxalate in solution by means of a strong acid.

It is probable that occlusion by other rare earth oxalates varies in the same way as in the case of neodymium.

(4) It is pointed out that the magnitude of the phenomenon is so great that the most reasonable explanation lies in the assumption of the existence of somewhat unstable double salts, rather than of true occlusion.

It seems probable also that the carrying down of the oxalates of sodium and potassium and of the other alkalies will vary with the conditions of precipitation as in the case of ammonium oxalate.

This question is now under investigation in this laboratory.

# ON THE CHROMATES OF MERCURY, BISMUTH AND LEAD.

By ALVIN J. COX.

Received June 30, 1906.

WHEN neutral salts are hydrolyzed, the reaction is reversible. By hydrolysis a neutral salt yields an acid or an alkaline solution as an equilibrium product. A neutral chromate of a heavy metal yields an acid solution. When the equilibrium is attained at a constant temperature the acid solution must assume a definite concentration.

It has already been shown<sup>1</sup> that the handbooks of chemistry contain descriptions, based on old literature, of basic salts that do not exist. There was formerly no theory to enable us to discriminate between a chemical compound and a mixture. Hence a great many mixtures have found their way into the literature as homogeneous substances.

In the previous paper only neutral and basic salts were studied. Of the acid salts of some of the heavy metals some have not been investigated at all and some but slightly. The use of the phase rule is also applicable to the identification and isolation of these.

The object of this study is to point out the conditions which are necessary to and which limit the existence of the chromates of the heavy metals—mercury, lead and bismuth.

The specific gravity of water solutions of chromium trioxide ( $\text{CrO}_3$ ) of definite percentage composition has been determined by Zettnow.<sup>2</sup> His data were taken at temperatures varying from  $9.7^\circ$  to  $35^\circ$ . In the majority of determinations, however, the temperatures lie between  $18^\circ$  and  $22^\circ$ , which we may assume as an ordinary range of room temperatures. He gives the following for a saturated water solution of chromium trioxide:

$\text{CrO}_3$ Per cent.	Sp. gr.	Gram-molecules per liter.	Temp.
62.23	1.7028	10.6	room

My results are the following:

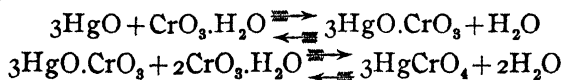
63.2 (saturated)	1.708	10.8	$25^\circ/4^\circ$
60.	1.667	10.	$25^\circ/4^\circ$

Let us consider the systems which can be built up from the three components, mercuric oxide, chromium trioxide and water.

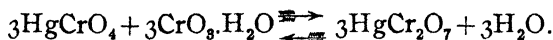
<sup>1</sup> Cox, A. J.: *Z. anorg. Chem.* **40**, 146 (1904).

<sup>2</sup> Zettnow: *Pogg. Ann.* **143**, 474 (1871); *Jsb.* 1871, 302.

The equilibriums:



have been studied<sup>1</sup> by considering the steps of hydrolysis of the neutral chromate. We can add to these a third, *viz.*:



In every reaction of this sort there is equilibrium of two opposing factors, the tendency to hydrolyze and the tendency to form complex salts. Each of these factors depends on the concentration of the acid, the former decreasing and the latter increasing with increasing concentration. When a system is in equilibrium these opposing factors are equal but as soon as one factor exceeds the other, reaction takes place.

The possibility of forming acid chromates of the heavy metals is limited only by the solubility of chromic acid. Experiment has shown that the tendency of mercuric bichromate to hydrolyze and its tendency to form from its components at 25° just balance when the concentration of chromium trioxide has very nearly reached its saturation point. If this value were greater than the saturation concentration, at that temperature no acid chromate would exist in equilibrium with a solution.

#### EXPERIMENTAL PART.

All experiments described in this paper were carried on at 25° by shaking in an electrically heated and electrically controlled thermostat.<sup>2</sup>

#### TABULAR ABBREVIATIONS.

W=The quantity of water in cubic centimeters which was added to the bottle.

t=The time of shaking in days.

G=The number of cubic centimeters of solution, which were removed for the analyses.

R=The difference between the number of cubic centimeters in the beginning and the number of cubic centimeters used for the analyses.

R'=R corrected for the change of volume produced by the addition or abstraction of chromium trioxide from the solution during the experiment.

<sup>1</sup> Cox: *Z. anorg. Chem.* 40, 146 (1904).

<sup>2</sup> Young, S. W.: *This Journal*, 23, 327 (1901).

The numbers calculated for  $25^{\circ}/4^{\circ}$  and used in this paper are as follows:

	Gram- molecules $\text{CrO}_3$ per liter.	Contains for each cc. Water in grams.
Saturated $\text{H}_2\text{CrO}_4$ .....	10.8	0.63
$(\text{H}_2\text{O}, \text{HgO})\text{CrO}_3$ [ $\text{CrO}_3$ and $\text{HgCr}_2\text{O}_7$ in equilibrium]..	11.42	0.606
$(\text{H}_2\text{O}, \text{HgO})\text{CrO}_3$ [ $\text{HgCr}_2\text{O}_7$ and $\text{HgCrO}_4$ in equilibrium].....	10.46	0.648
$(\text{H}_2\text{O}, \text{Bi}_2\text{O}_3)\text{CrO}_3$ [ $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ and $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ in equilibrium] .....	7.8	0.747
$(\text{H}_2\text{O}, \text{PbO})\text{CrO}_3$ [ $\text{PbCr}_2\text{O}_7$ and $\text{PbCrO}_4$ in equilibrium]	6.87	0.78
$(\text{H}_2\text{O}, \text{PbO})\text{CrO}_3$ [ $\text{CrO}_3$ and $\text{PbCr}_2\text{O}_7$ in equilibrium]..	10.8	0.63

$n$  = The titration value of 1 cc. of the solution in cubic centimeters of  $\text{N}/_{10} \text{FeSO}_4$ .

$m$  = Gram-molecules  $\text{CrO}_3$  per liter.

Hg, Bi, Pb, etc. = Grams Hg, Bi, Pb, etc., in 1 cc. solution.

$\text{Hg}'$ ,  $\text{Bi}'$ , etc. = Gram-molecules Hg, Bi, etc., per liter.

$q$  = The ratio of  $\text{HgO}$ ,  $\text{Bi}_2\text{O}_3$ , etc., to acid residue in the solid phases.

#### METHOD OF ANALYSIS.

With the exception of those of lead, the chromates investigated are all soluble in sulphuric acid. The chromium trioxide could therefore be at once determined by titration with ferrous sulphate solution, using potassium ferricyanide as indicator.

The chromates of lead are soluble in sodium hydroxide. To such a solution an excess of ferrous sulphate was added, the solution then acidified with sulphuric acid and titrated with standard potassium bichromate solution.<sup>1</sup>

The other metals were precipitated and weighed as sulphides.<sup>2</sup>

#### MERCURIC BICHROMATE.

In two preliminary experiments  $1/10$  gram-molecule mercuric oxide (Kahlbaum's preparation),  $43/100$  gram-molecule chromium trioxide and 25 cc. of a saturated solution of chromium trioxide; and  $1/10$  gram-molecule mercuric oxide,  $2/10$  gram-molecule chromium trioxide and 25 cc. of a saturated solution of chromium trioxide, respectively, were shaken together in 50 cc. flasks.<sup>3</sup> The data and results are contained in the following table:

<sup>1</sup> This might easily be adapted to the volumetric determination of lead

<sup>2</sup> Treadwell-Hall: Quant. Anal. Vol. II, 133, 141.

<sup>3</sup> The results were saturated solutions of  $\text{CrO}_3$ , saturated with mercuric bichromate; in other words, solutions in equilibrium with  $\text{CrO}_3$  and mercuric bichromate as solid phases.



TABLE I.

	No.	l.	W.	G.	R.	R'.	$\pi$ .	$m$ . <sup>1</sup>	Sp. gr.
1.....	1	1	0	5	20	21.2	343	11.43	1.8888
2.....	2	2	0	5	20	21.2	342	11.41	1.888

To the remainder from Expt. 2 pure neutral mercuric chromate<sup>2</sup> was added in sufficient quantity to combine with the free acid in excess of the equilibrium concentration of mercuric bichromate. The product was the formation of more acid chromate as follows:

Mercuric chromate + chromium trioxide  $\rightleftharpoons$  mercuric bichromate.

The data and results are given in the following table:

TABLE II.

No.	Weight of HgCrO <sub>4</sub> added in grams.	l.	G.	R.	R'.	$\pi$ .	$m$ .	Hg.	Hg'.	$\frac{g}{\text{HgO} : \text{CrO}_3}$ .
				21.2						
						Liquid phase constant.				2 solid phases.
1.....	25	1	2	19.2	18.4	313.7	10.46	.....	.....	3 : 3.8
2.....	8	2	2	16.2	16.4	313.8	10.46	1517	0.7585	3 : 3.6

From the foregoing data we see that the reaction mercuric chromate + chromium trioxide  $\rightleftharpoons$  mercuric bichromate is in equilibrium when the solution contains 10.46 gram-molecules chromium trioxide ( $[\text{H}_2\text{O}, (\text{HgO})_x]\text{CrO}_3$ ) per liter, *i. e.*, at this concentration the tendency to hydrolyze just balances the tendency toward the formation of complex salts.

With these data at hand the preparation and identification of mercuric bichromate were not difficult. The remainder from Expt. 1, Table I, was used as a starting point. The supernatant liquid was decanted off and the solid phases, which consisted of acid mercuric chromate and free chromic acid, were washed with a solution of the above-mentioned concentration, *viz.*, 10.46 gram-molecules  $\text{CrO}_3([\text{H}_2\text{O}, (\text{HgO})_x]\text{CrO}_3)$  per liter, until all of the free chromic acid was washed out, *i. e.*, until the wash liquid no longer increased in chromium trioxide content when shaken with the solid phase.

The salt which was of a deep crimson color was pressed between absorption plates and thoroughly dried at 65°. This substance upon analysis gave 50.2 per cent.  $\text{CrO}_3$ ; calculated for  $\text{HgCr}_2\text{O}_7$ , 48.1 per cent.

<sup>1</sup> Gram-molecules  $[\text{H}_2\text{O}, (\text{HgO})_x]\text{CrO}_3$ .

<sup>2</sup> Geuther: Ann. 106, 244; Cox: Loc. cit. p. 150.

A high result is to be expected in view of the fact that the wash liquid is almost a saturated solution of chromic acid.

The concentration of chromium trioxide lying between that concentration which represents the hydrolytic dissociation pressure of chromium trioxide for mercuric bichromate and for neutral mercuric chromate was investigated.

In a 90 cc. bottle were placed 33.79 grams chromium trioxide and 25.9 grams mercuric oxide (Kahlbaum) and to these were added 30 cc. of a solution saturated with respect to mercuric bichromate and chromic acid as described in Expt. 1, Table I. The data and results are contained in the following table:

TABLE III.

No.	W.	<i>t</i> .	G.	R.	R'.	<i>n</i> , Liquid phase constant. <sup>1</sup>	<i>m</i> .	Hg.	Hg'.	$\frac{q}{\text{HgO} \cdot \text{CrO}_3}$	
1	0			30	30.	342.3	11.41				3 : >6
2	5	1	5	30	33.3	342.0	11.4				3 : >6
							11.				3 : 6
							10.46				3 : 6
											2 solid phases
3	5	$\frac{1}{2}$	5	30	34.2	310.8 <sup>1</sup>	10.36				3 : 5.30
4	5	2	5	30	37.	313.0 <sup>1</sup>	10.43	0.1517	0.7585		3 : 3.16
						Liquid phase variable.					1 solid phase of constant composition. Stable.
5	2	2	5	27	34.2	297.0	9.90				3 : 3
6	0	2	5	22	29.2	296.8	9.89				3 : 3
7	15	2	10	27	34.2	201.9	6.73				3 : 3
8	10	2	5	32	39.2	156.0	5.20				3 : 3
9	10	4	5	37	44.2	124.8	4.16				3 : 3
10	20	1	5	52	59.2	87.0	2.90				3 : 3
11	20	4	30	42	49.2	62.4	2.08				3 : 3
12	20	1	15	47	54.2	43.5	1.45				3 : 3
13	20	1	10	52	64.2	30.8	1.035				3 : 3

The table is continued from results at 50° C. already published.<sup>2</sup>

50	3	5		45		30.01	1.006	0.0203	0.1		3 : 3
	5	1	5	45		27.06	0.907	0.0185	0.092		3 : 3
	10	1	5	50		22.11	0.740	0.0145	0.072		3 : 3

<sup>1</sup> The value of *n* or *m* is a little small, depending upon *t*. These reactions reach equilibrium rather slowly, c. f. Table II.

<sup>2</sup> Z. anorg. Chem. 40, 158, Tabelle VII; 152, Tabelle II (1904).

TABLE III (continued)

No	W	l	G	R	R'	n	m	Hg	Hg'	$\frac{q}{\text{HgO CrO}_3}$	1 solid phase of constant composition
						Liquid phase variable				Labile	
5	1		5		50	20 39	0 683	0 0142	0 071	3	3
5	2		5		50	18 48	0 620	0 0132	0 066	3	3
5	2		5		50	17 41	0 583	0 0122	0 061	3	3
5	1		5		50	16 29	0 546	0 0111	0 055	3	3
5	1		5		50	15 58	0 522	0 0101	0 050	3	3
5	1		5		50	14 91	0 499	0 0098	0 049	3	3
						Liquid phase constant				2 solid phases in varying relative masses	
28	3	0 5	18	3	10	20 85	0 699		0 0745	3	2 49
10	2		10		10	21 50	0 720		0 0745	3	2 22
10	1		10		10	22 03	0 737		0 0745	3	1 95
10	1		10		10	20 85	0 698		0 0745	3	1 68
10	3		5		15	21 02	0 705		0 0745	3	1 39
10	2		10		15	21 39	0 716	0 0149	0 0745	3	1 15
						Liquid phase variable				1 solid phase of constant composition	
10	2		5		20	17 29	0 580	0 0102	0 0510	3	1
10	2		5		25	11 10	0 371	0 0045	0 0225	3	1
5	4		5		25	9 14	0 306	0 0030	0 0150	3	1
5	2		5		25	7 58	0 254	0 0024	0 0120	3	1
15	2		10		30	4 58	0 154	0 00072	0 0036	3	1
60	3		40		50	1 31	0 0440	0 00020	0 0010	3	1
50	3		75		25	0 43	0 0144	0 00010	0 0005	3	1
75	3		70		35	0 14	0 0047	0 00003	0 00015	3	1
70	5		105		0	0 041	0 00137			3	1
						Liquid phase constant				Two solid phases	
110	2		110		0	0 0036	0 00012			3	0 9994
110	3					0 0036	0 00012			3	0 9988

After Expt 13, Table III, some of the solid phase which was of a light orange color was isolated, pressed between absorption plates and thoroughly dried. It gave 31.6 per cent.  $\text{CrO}_3$ , calculated for  $\text{HgCrO}_4$ , 31.66 per cent.

This leaves no doubt as to its formula and as to its being the same salt as that used in the other experiments

The hydrolytic dissociation pressure of chromium trioxide for neutral mercuric chromate at  $25^\circ$  corresponds to 0.456 gram-molecule per liter. The basic mercuric chromate which has the formula  $3\text{HgO} \cdot \text{CrO}_3$  is a dark red powder.



When we plot the results of Table III, the above curve is obtained:

#### LEAD BICHROMATE.

It has already been shown that a bichromate is formed from a chromate and free chromic acid. Bichromates in solution are in general strongly acid toward litmus and act as strong acids toward many substances. This is made clear by the known fact that from a solution of bichromate, monochromate may be precipitated.<sup>1</sup> By the addition of water to such a solution very often a precipitate of a more basic salt forms immediately. It is clear that in the solution there are not only bichromate ions but also monochromate ions and therefore free chromic acid. These general remarks find a good illustration in the lead salt,  $\text{PbCr}_2\text{O}_7$ . In the literature we find such statements as this: "With water lead bichromate decomposes with the formation of lead chromate."<sup>2</sup>

Lead bichromate was prepared by grinding 1 gram-molecule of lead oxide with  $2\frac{1}{2}$  gram-molecules of chromic anhydride and enough saturated solution of chromium trioxide to cause it to triturate easily. The lead bichromate thus formed and the excess of chromium trioxide were shaken in the thermostat with a saturated solution of chromium trioxide to obtain the equilibrium constant of the system  $\text{PbCr}_2\text{O}_7, \text{CrO}_3$ . The data and results are as follows:

TABLE IV.

No.	<i>l</i> .	W.	G.	R.	<i>n</i> .	<i>m</i> .	Pb.	Sp. gr.	$\frac{g}{\text{PbO} \cdot \text{CrO}_3}$
I	I.5	...	5	...	323.7	10.79	small	I.716	I : < 2

Preliminary experiments showed lead bichromate to be stable in a solution of chromium trioxide as dilute as 7 *m*. The salt was obtained pure by dissolving out the free chromium trioxide and washing with 7 *m* chromium trioxide solution. The salt was pressed thoroughly between absorption plates and allowed to stand for a long time in a desiccator over calcium chloride. The salt upon analysis gave 47.14 and 47.09 per cent.  $\text{CrO}_3$ ; calculated for  $\text{PbCr}_2\text{O}_7$ , 47.32 per cent.

This salt is a brick-red crystalline powder. Under the microscope the crystals appeared very uniform and pure.

Twenty-five grams of the above analyzed lead bichromate were weighed into a 40 cc. bottle and 20 cc. of a solution of chromium

<sup>1</sup> Abegg and Cox: *Z. physik. Chem.* 48, 725 (1904).

<sup>2</sup> Preis and Raymann: *Ber.* 13, 340.

trioxide saturated with lead bichromate and which showed a content of 8.196 *m* chromium trioxide were added. The data and results are given in the following table:

TABLE V.

No.	W.	<i>t</i> .	G.	R.	R'.	<i>n</i> .	<i>m</i> .	Pb <sup>1</sup> $\frac{g}{PbO:CrO_3}$
						Liquid phase variable.		1 solid phase.
1	0	2	1	19	19	245.9	8.196	1 : 2
						Liquid phase constant.		2 solid phases.
2	4	2	1	22	22.1	206.0	6.865	1 : 1.96
3	6	2	1	27	28.8	206.0	6.865	1 : 1.08
						Liquid phase variable.		1 solid phase of constant composition.
4	4	20	4	27	28.9	181.2	6.04	1 : 1
5	6	5	11	22	23.9	147.0	4.90	1 : 1
6	15	1	20	17	18.9	88.5	2.95	1 : 1
7	25	1	25	17	18.9	36.6	1.22	1 : 1
8	25	1	25	17	18.9	14.82	0.494	1 : 1
9	25	2	25	17	18.9	6.12	0.204	1 : 1
10	25	1	25	17	18.9	2.46	0.082	1 : 1
11	25	1	25	17	18.9	1.02	0.034	1 : 1
12	25	1	25	17	18.9	0.38	0.0127	1 : 1
13	500	1	500	17	18.9	0.0015	0.0005	1 : 1
						Liquid phase constant.		2 solid phases
14	500	2	500	17	18.9	0.0006	0.00002	1 : > 1
15	500	2	500	17	18.9	0.0006	0.00002	1 : > 1

Undeterminably small.

The method here employed is not applicable to the identification of the basic chromates of lead. When lead chromate and lead oxide are mixed in the presence of water there is a large swelling of the volume of the solid phases which is undoubtedly the result of the formation of a basic salt, probably  $2PbO \cdot CrO_3$ , commonly known as chrome red.

$3PbO \cdot CrO_3$  exists in nature as the mineral melanochroite, phoenicochroite and is also described by Herman.<sup>2</sup>

After Expt. 12, Table V, some of the solid phase was isolated, pressed between absorption plates, and thoroughly dried. It gave 30.81 and 30.85 per cent.  $CrO_3$ ; calculated for  $PbCrO_4$ , 30.99 per cent.

When the results in Tables IV and V are plotted the following

<sup>1</sup> Calculated from electrical conductivity measurements of  $PbCrO_4 + Aq$ ; 1 liter dissolves 0.2 mg.  $PbCrO_4$  at 18° C. Kohlrausch and Rose: Z. physik. Chem. 12, 241.

<sup>2</sup> Pogg. Ann. 28, 162.

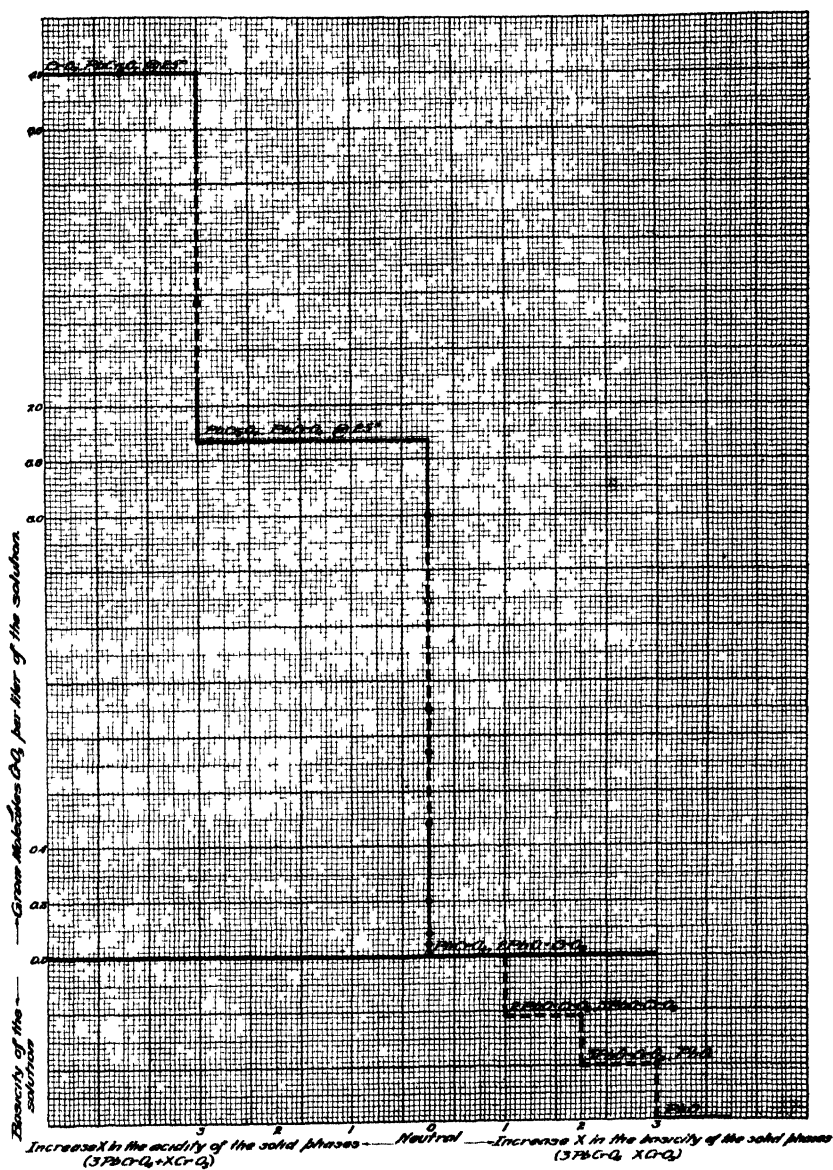


Fig 2

curve is obtained, which shows conclusively that no salt exists between the bichromate and monochromate of lead.

#### BISMUTH CHROMATE.

Neutral bismuth chromate is unknown. There is a salt with a third less chromium trioxide than that corresponding to the neutral chromate and one with a third more. The latter, the highest chromate of bismuth, was prepared by grinding together bismuth oxide and chromium trioxide in the molecular relations of one to slightly more than four, with just enough saturated chromium trioxide solution to make a paste. Afterwards, by the careful addition of water, it was possible to dissolve the grains of free acid and reach a dilution of chromium trioxide with which this bismuth salt was in equilibrium. This at room temperature is somewhat less than 8 gram-molecules per liter or a solution of sp. gr. = 1.5.

Some of the salt prepared as above described was removed from the 8 *m* chromium trioxide solution to an absorption plate, allowed to stand twenty-four hours and finally dried and analyzed. No special precautions were taken to free the sample from mother-liquor and the analyses are therefore high with regard to chromium trioxide but are interesting from the standpoint of a "Note on the Efficiency of Centrifugal Purification,"<sup>1</sup> when compared with two other pairs of analyses of the same salt given below.

The analysis gave 46.6 and 46.8 per cent.  $\text{CrO}_3$ ; calculated for  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , 46.3 per cent.

In order to determine the hydrolytic dissociation pressure of the chromium trioxide from  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , 20 grams of the above analyzed salt were shaken with 25 cc. of the mother-liquor = 7.5 *m* chromium trioxide. The data and results are as follows:

TABLE VI.

No.	W.	<i>t</i> .	G.	R.	R'.	<i>n</i> .	<i>m</i> .	Bi.	Bi'.	$\frac{q}{\text{Bi}_2\text{O}_3 : \text{CrO}_3}$ 2 solid phases.
						Liquid phase constant.				
1	0	1	1	24	24¼	232.2	7.74	0.016	0.04	1 : 3.4
2	0	2	1	23	23¼	233.8	7.794	0.016	0.04	1 : 3.3
3	10		0	33	34½					1 : 2

The salt being completely hydrolyzed according to the reaction  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3 \rightleftharpoons \text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3 + 2\text{CrO}_3$ , 8 grams of  $\text{CrO}_3$  were added so as to approach the

<sup>1</sup> T. W. Richards: This Journal, 27, 104 (1905).



equilibrium from the other direction as shown by the reaction  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3 + 2\text{CrO}_3 \rightleftharpoons \text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ .

4   0   3<sup>1</sup>   1   ...   36½   234.0   7.80   0.016   0.04   1 : 2.5

The hydrolytic dissociation pressure of chromium trioxide from  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  is 7.794–7.80 *m*. With these data at hand the purest possible  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  was obtained. Twenty-five grams of the above analyzed salt and 22 cc. of a solution of chromium trioxide saturated at 25°, which analyzed 10.76 *n*, were placed in a 50 cc. bottle. The data and results are contained in the following table:

TABLE VII.

No.	W.	<i>t</i> .	G.	R.	" Liquid phase variable.	<i>m</i> .	Bi.	Bi'.	$\frac{g.}{\text{Bi}_2\text{O}_3 : \text{CrO}_3.}$ 1 solid phase.
1	0	6	2	20	335.4	11.17	0.04	0.1	1 : 4
2	5	3	2	23	267.8	8.93	.....	.....	1 : 4
3	3	3	1	25	237.4	7.92	0.016	0.04	1 : 4

The last dilution carries the concentration of the chromium trioxide close to the equilibrium point and it is as far as it is safe to go.

It is evident that the only wash liquid permissible for this salt is a solution of chromium trioxide containing not less than 7.8 gram-molecules per liter. If it is possible to free the salt from the mother-liquor, it is then in the pure form. Two methods were tried, *viz.*; first, by pressing with a very considerable pressure between clay absorption plates for some hours; second, by centrifuging in a platinum basket for a few hours and finally in both cases drying over calcium chloride. Sulphuric acid as a drying agent was tried, but as it caused the salt to decolorize somewhat the method was abandoned.

The sample obtained by the first method gave 46.0 and 46.2 per cent.  $\text{CrO}_3$ ; calculated for  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , 46.3 per cent.

This sample may have been contaminated with a very small trace of basic chromate as the pressing had to be done in the open air. The small amount of mother-liquor ( $\text{CrO}_3$ ) would attract moisture from the air until its concentration was lowered below the hydrolytic dissociation pressure for  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , whereby a small amount of  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  was hydrolyzed and the chromium trioxide liberated absorbed in the plates together with the mother-liquor.

<sup>1</sup> By a series of experiments it has been ascertained that equilibrium is complete in forty-eight hours, but a period of three days has been consistently used in order that there may be no question.

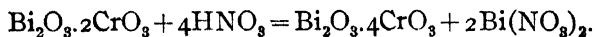
The sample obtained by the second method gave, upon analysis, 46.2 and 46.3 per cent.  $\text{CrO}_3$ ; 54.1 and 53.8 per cent.  $\text{Bi}_2\text{O}_3$ ; calculated for  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , 46.3 and 53.7 per cent.

This salt is a splendid orange vermillion and when perfectly dry is fairly stable in the air.

Muir<sup>1</sup> undoubtedly obtained the same salt, to which he assigned the formula  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3 \cdot \text{H}_2\text{O}$ . I cannot but doubt the accuracy of his numbers. His sample was probably not perfectly dry. Even the analyses from which he makes his deductions contain only two-thirds of the water necessary to make up the theoretical amount.

This salt, as is to be expected, may be formed by boiling the lower chromate with nitric acid.

The reaction might be represented as follows:



The reaction  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3 + 2\text{CrO}_3 \xrightleftharpoons[\text{acid}]{\text{conc.}} \text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  is dependent on the acid concentration. If part of this concentration is made up of nitric acid, it is equally effective. In the same manner the hydrolysis of  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  will not take place in a solution of chromic acid less than 7.8 *m* if the required acid concentration is made up of nitric acid.

Table VII begins with the concentration where chromium trioxide and  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  are in equilibrium and the concentration of the chromium trioxide is variable in direct proportion to the dilution. To have that degree of freedom there could have been but one solid phase. This shows therefore that  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  is the highest chromate of bismuth. The possibility of bichromate is excluded, owing to the limited solubility of chromium trioxide which makes it impossible to attain the hydrolytic dissociation pressure of such a salt.

Starting with  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ , it is possible to isolate and analyze the more basic chromates. To do this 50 grams of the above analyzed salt were weighed into a 100 cc. bottle and a solution of chromium trioxide saturated with  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  at room temperature was added. The data and results are given in the following table:

<sup>1</sup> J. Chem. Soc. 30, 17 (1876).

TABLE VIII.

No.	W.	l.	G.	R.	R'.	n.	m.	Bi.	Bi'.	$\frac{q}{p}$ Bi <sub>2</sub> O <sub>3</sub> :CrO <sub>3</sub> 1 solid phase.
				40	40.	229.6	7.66 <sup>1</sup>	0.016	0.04	1:4
						Liquid phase constant.				2 solid phases.
1	0	10	2	38	38.	233.5	7.783	0.016	0.04	1:3.9
2	4	3	2	40	41.36	233.8	7.793	0.016	0.04	1:3.18
3	2	7	2	40	42.04	234.2	7.807	0.016	0.04	1:2.82
4	4	5	2	42	45.40	234.3	7.810	0.016	0.04	1:2.11
						Liquid phase variable.				1 solid phase of constant composition.
5	4	4	2	44	48.75	216.5	7.22			1:2
6	0	3	2	42	46.75	216.6	7.22			1:2
7	4	10	2	44	48.75	198.6	6.62			1:2
8	20	4	25	39	43.75	140.0	4.666			1:2
9	25	2	25	39	43.75	88.0	2.933			1:2
10	42	2	57	24	28.75	44.1	1.470			1:2
11	50	2	40	34	38.75	16.05	0.535			1:2
12	40	2	20	54	58.75	7.89	0.263			1:2
13	20	2	30	44	48.75	5.88	0.196			1:2
14	30	2	40	34	38.75	3.57	0.119			1:2
15	40	2	45	29	33.75	1.64	0.058			1:2
16	50	1	35	44	48.75	0.69	0.023			1:2
17	40	2	45	39	43.75	0.39	0.013			1:2
18	45	2	60	24	28.75	0.18	0.006			1:2
19	60	2	55	29	33.75	0.06	0.002			1:2
20	55	2	60	24	28.75	0.018	0.0006			1:2
21	60	2	75	9	13.75	0.006	0.0002			1:2
						Liquid phase constant.				2 solid phases.
22	400	2	400	9	13.75	0.0003	0.00001			1:>2
23	400	2	400			0.0003	0.00001			1:>2

Undeterminably small.

After Expt. 20 some of the salt was removed and thoroughly dried. It was found to contain no water. It analyzed as follows: CrO<sub>3</sub>, 30.14 and 29.95 per cent.; Bi<sub>2</sub>O<sub>3</sub>, 70.02 per cent.; calculated for Bi<sub>2</sub>O<sub>3</sub>.2CrO<sub>3</sub>, 30.1 and 69.9 per cent.

This salt is an orange-yellow. This formula Bi<sub>2</sub>O<sub>3</sub>.2CrO<sub>3</sub> was assigned by Löwe<sup>2</sup> who has described this salt very accurately.

A large number of chromates of bismuth have been described in the literature, but many of them can probably be classified as impure specimens of one or the other of these salts or mixtures.

<sup>1</sup> Room temperature.

<sup>2</sup> J. pr. Chem. 67, 463 (1856).

The salts  $3\text{Bi}_2\text{O}_3 \cdot 7\text{CrO}_3$  and  $5\text{Bi}_2\text{O}_3 \cdot 11\text{CrO}_3$  described by Muir<sup>1</sup> are undoubtedly impure samples of  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ .

Pearson<sup>2</sup> has even assigned the formula  $\text{Bi}_2\text{O}_3 \cdot \text{CrO}_3$  to this ordinary orange-yellow salt which is obtained by precipitating bismuth nitrate with potassium dichromate but the accuracy of his numbers has already been doubted.<sup>3</sup>

The salt described by Löwe,<sup>3</sup> to which he assigns the formula  $3\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ , may be, judging from his method of preparation and in the light of the present investigation, a mixture of  $\text{Bi}_2\text{O}_3 \cdot \text{CrO}_3$  and  $\text{Bi}_2\text{O}_3$ . Owing to the practically zero or perhaps negative value for the hydrolytic dissociation of  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ , the methods employed in this research are not applicable to the identification of the chromates of bismuth containing less  $\text{CrO}_3$  than  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ . As for those containing more  $\text{CrO}_3$  than  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$  there exists at  $25^\circ$  but the one, *viz.*,  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ . The salt described by Pearson<sup>4</sup> as  $\text{Bi}_2\text{O}_3 \cdot 3\text{CrO}_3$  is undoubtedly an impure specimen of this salt.

When the results of Tables VII and VIII are plotted, the following curve is obtained, which shows the relationship which exists between these two salts.

#### SUMMARY.

(1) By investigations from the standpoint of the phase rule, it is possible to distinguish the existing salts from the mixtures of two salts in undefined proportions which have found their way into the chemical literature as chemical compounds.

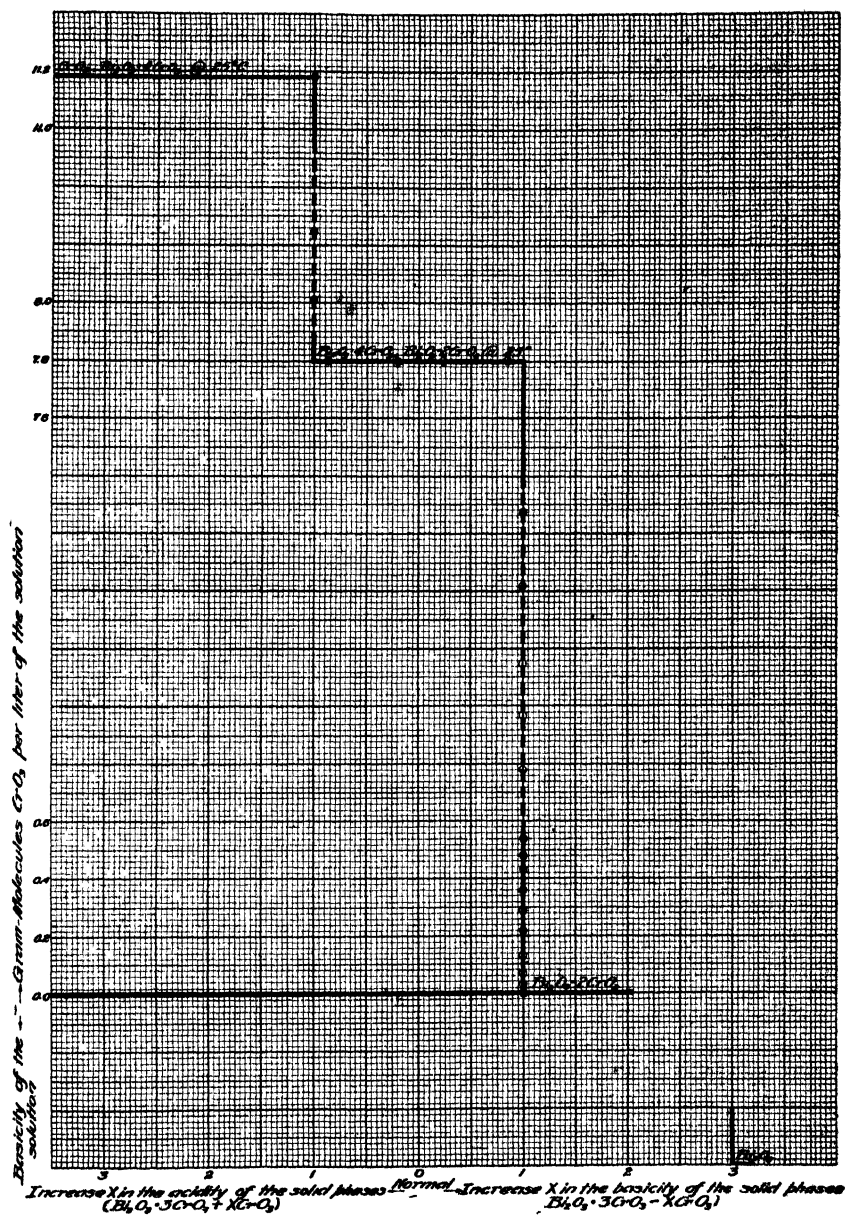
(2) The phase rule states that the number of components less the number of phases plus two equals the number of degrees of freedom. Systems like those under discussion in this paper when two solid phases are present have one degree of freedom. The components are: the oxide of the heavy metal; chromium trioxide and water. The phases are: two chromates, solution, and vapor. It is only necessary to work at constant temperature to attain complete equilibrium. At constant temperature the only possible variation from the state of equilibrium is in the disappearance of one of the chromates (one solid phase), at which

<sup>1</sup> J. pr. Chem. 31, 24 (1877).

<sup>2</sup> Phil. Mag. [4], 11, 204.

<sup>3</sup> J. pr. Chem. 67, 288 (1856).

<sup>4</sup> Pearson: Phil. Mag. [4], 11, 206.



**Fig. 3.**

time the concentration of the solution will become variable in direct proportion to its dilution, or we can state conversely that at constant temperature, the changing of the acid concentration in proportion to the dilution is indicative of one and only one solid phase—one chemical individual.

(3) The two highest chromates of mercury, lead and bismuth, are respectively  $\text{HgCr}_2\text{O}_7$ ,  $\text{HgCrO}_4$ ,  $\text{PbCr}_2\text{O}_7$ ,  $\text{PbCrO}_4$ ,  $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$  and  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ .

(4) In accord with the phase rule each of these salts has a certain hydrolytic dissociation pressure, i. e., a certain minimum acid concentration below which it is not stable. Without a knowledge of these concentrations it is not, in general, possible to prepare the salts pure.

The hydrolytic dissociation pressures for the above salts in gram-molecules of  $\text{CrO}_3$  per liter at  $25^\circ$  are:

1. $\text{HgCr}_2\text{O}_7$ .....	10.46
$\text{HgCrO}_4$ .....	0.46
2. $\text{PbCr}_2\text{O}_7$ .....	6.87
$\text{PbCrO}_4$ .....	0.00002
3. $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ .....	7.80
$\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ .....	0.00001

All of these salts require an acid of the above concentration as a minimum for their formation and to maintain their stability.

(5) The existence in the pure form of the second highest chromates is limited by a maximum acid concentration equal to the minimum concentration of the next higher chromate, while the existence of the highest chromates is limited only by their own solubility and that of chromium trioxide. This is easily seen from the figures in the text.

IRELAND STANFORD, JR., UNIVERSITY, CALIF.,  
March, 1906

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[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY OF  
NEW YORK UNIVERSITY.]

## THE CHANGE FROM GREEN TO VIOLET IN CHROMIUM CHLORIDE SOLUTION.

BY ARTHUR B. LAMB.

Received October 27, 1906.

Weinland and Koch<sup>1</sup> have recently disclosed some interesting facts regarding the precipitability of the chlorine in the green

<sup>1</sup> Weinland and Koch: Z. anorg. Chem. 39, 256, (1904).

hydrate of chromic chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , by silver salts. Working first *without* the addition of acid they found that while silver salts of strong acids do *not* produce complete precipitation, even when present in great excess, silver salts of very weak acids, added in equivalent amounts, produce immediate and complete precipitation. They are at a loss to explain this unusual phenomenon, and point out that this is the first instance known, where, the *anion* influences the reactions of its cation. In what follows, I think there will be found a plausible explanation of this unexpected behavior.

Godefroy<sup>1</sup> and Recoura<sup>2</sup> early observed that hydrochloric acid, when added to solutions of the green chloride of chromium, retards the change to the violet modification. Weinland and Koch,<sup>3</sup> in studying the precipitability of the green chloride in *acid* solution, obtained results agreeing with this observation. They found that strong acids, such as nitric, chloric, perchloric and permanganic, can prevent the precipitation of two of the three chlorine atoms; sulphuric and lactic acids can hinder the precipitation to a somewhat less extent, while acetic acid can only prevent the precipitation of a single atom of chlorine. Evidently then, the stronger the acid, or in other words, the greater the concentration of the hydrogen ion, the less the precipitation. Now the increasing precipitability of the green salt is undoubtedly due to its gradual reversion to the completely precipitable violet modification. Whatever, then, hinders this change is unfavorable to complete precipitation. That hydrogen ions do lessen the precipitability is therefore in precise accordance with the observation of Godefroy and Recoura.

I have tested the effect of hydrogen ions on the rate of change of the green into the violet modification in a somewhat more exact manner, by following the change in the electrical conductivity of the solutions, Werner and Gubser<sup>4</sup> having shown that the green and the violet modifications have very different molecular conductivities.

Curve I shows the rate of change of the conductivity with the time when the solution contained nothing but the chromic chlo-

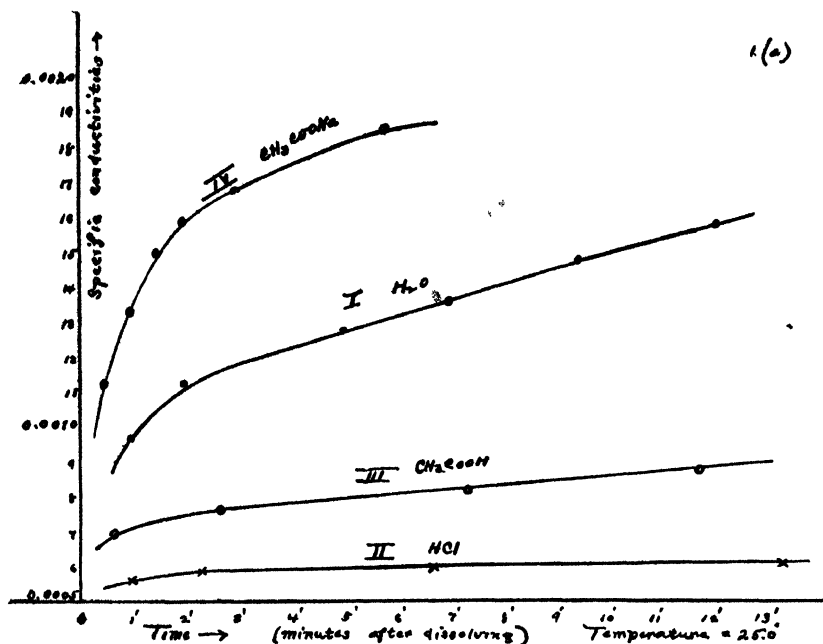
<sup>1</sup> Godefroy: Compt. rend. 100, 105 (1885).

<sup>2</sup> Recoura: Ann. chim. phys. [6] 10, 37 (1887).

<sup>3</sup> Weinland and Koch: Loc. cit.

<sup>4</sup> Werner and Gubser: Ber. 34, 1597 (1901).

ride. Curve II shows the change when an approximately equivalent amount of hydrochloric acid was present. Curve III shows the same thing when a considerable excess (20 times) of acetic acid was present.<sup>1</sup>



It is seen that a marked paralysis of the change is produced by the addition of the strong acid and a much slighter one by the addition of the weak acid. I now dissolved the chloride in an approximately equivalent solution of sodium acetate. In this solution the concentration of the hydrogen ion must have been

<sup>1</sup> The solutions were all N/125 as regards chromic chloride. The hydrochloric acid and the acetic acid solutions were N/125 and N/6, respectively, as regards the acids themselves.

The specific conductivities represent the differences between the specific conductivities of the solution before and after the addition of the chromic chloride.

The addition of the sodium acetate not only accelerated the change but altered the location of the equilibrium. The specific conductivity never got much beyond 0.00200; that is, the final equilibrium was reached in an hour, while in pure water equilibrium is only reached after a day or more.

It is entirely an open question whether the conductivity is a linear function of the concentrations of the two kinds of chromium. This question does not, however, affect a *comparison* such as is here made.



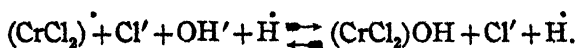
even smaller than in pure water, because of the relatively high concentration of the action. The change ought here then to be *more rapid* than in pure water. Curve IV shows that this was indeed the case.

From these experiments, the observation of Godefroy and Re-coura and the experiments of Weinland and Koch in acid solution, it seems reasonable to conclude that the concentration of the hydrogen ion has a marked influence on the rate of the color change, but what is still more convincing is that the previously inexplicable variable precipitating power of the different silver salts in neutral solution as observed by Weinland and Koch and referred to above is easily explicable on this basis.

Chromic chloride solutions of themselves contain a definite concentration of hydrogen ions, depending on the concentration of the solution and the temperature; that is, they are hydrolyzed. When a silver salt is added to such a solution an equilibrium must be established between the hydrogen ions in solution and the anions of the added salt. The location of this equilibrium is determined, since other factors are constant, by the dissociation constant of the acid from which the silver salt is derived. The weaker the acid the less the concentration of hydrogen ion compatible with a given concentration of the anion, and the concentration of the anion is relatively large. It follows that the weaker the acid from which the added silver salt is derived, the less will the transformation into the violet modification be retarded and hence the *greater will be the amount of chlorine precipitated*. This is, as we have seen, precisely what Weinland and Koch found to be the case.

The only explanation which I have as yet been able to frame for this striking action of the hydrogen ion, is that one step in the process of isomerization is the formation of a *hydrolyzed derivative* of chromic chloride. Now in the case of a salt like chromic chloride there are two possible sorts of hydrolysis, due to the fact that there are two sorts of chlorine atoms present, the precipitable and the non-precipitable.

The first sort of hydrolysis would be of the usual electrolytic type. The complex cation would unite with the hydroxyl ion to form the undissociated base.



At equilibrium the concentration of the base would evidently be directly proportional to the concentration of the hydroxyl ion and hence through the equilibrium with water of constant concentration inversely proportional to the concentration of the hydrogen ion. If this hydrolyzed derivative were the compound which actually changed over to the violet modification, and if this change were the slow step in the whole process, then the velocity of the color change as a whole would be proportional to the concentration of the hydroxyl ion and therefore inversely proportional to the concentration of the hydrogen ion. This then would explain the observed retarding effect of hydrogen ions on the color change and on precipitation.

The same can be said of the second sort of hydrolysis. Here the hydroxyl ion, always present in aqueous solution, substitutes for both chlorine atoms in the *complex*, the chlorine ion requiring the negative charge of the hydroxyl ion. We may either consider that this in itself destroys the green complex, or what amounts to practically the same thing, that the green instantly changes to the violet modification, with accompanying instantaneous dissociation of the hydroxyl ions. The formation of the hydroxyl compound would then be the slow step in the whole process of isomerization, and since its velocity would be directly proportional to the concentration of the hydroxyl ions (or to the square of their concentration) and therefore inversely proportional to the concentration of the hydrogen ions, the velocity of the whole process would itself be inversely proportional to the concentration of the hydrogen ion. Both sorts of hydrolysis then would give results in accordance with the observations.

Both sorts of hydrolysis undoubtedly take place in aqueous solutions of chromic chloride. But there are reasons for believing that the latter sort of hydrolysis probably constitutes the essential, efficient step in the transformation of the green modification into the violet. Thus Pfeiffer<sup>1</sup> found that with certain pyridine derivatives of the hexahydrates of chromic chloride and bromide, when treated with pyridine or ammonia, yielded a precipitate of hydroxy-chloride or -bromide, and that this precipitate, if allowed to remain in contact with the precipitant, changed its color, and when redissolved in acids gave violet solutions. Acids and alkalis have a similar effect on the interconversion of the roseo and

<sup>1</sup> Pfeiffer: Ber. 39, 1879 (1906).

purpureo ammonio salts of chromium. Recoura,<sup>1</sup> long ago, observed a similar behavior when ordinary green chromic chloride was treated with alkalis. Furthermore, Pfeiffer<sup>2</sup> found that a yellowish green isomer of the above pyridine derivatives was similarly changed into the violet modification by the action of pyridine or ammonia, although none of its chlorine was precipitable with silver nitrate, which in this case, at least, precludes the first sort of hydrolysis.

From this point of view, the color change in pure aqueous solutions of green chromic chloride would become a rather interesting type of reaction. The hydrolysis of the chlorine ions in the green complex would be taking place in a solution whose hydroxyl ion concentration, and consequently whose hydrogen ion concentration, would be governed by the degree of hydrolysis of the green complex ion,  $(CrCl_2')$  disappearing, and of the violet ion  $(Cr'')$  being formed. If the latter were less hydrolyzed than the former, the hydrogen ion concentration would *decrease*, as the color change progressed, and we should have a case of auto-catalysis. If, on the other hand, the latter were more hydrolyzed, the concentration of the hydrogen ion would *increase* and we should have a case of *negative* auto-catalysis.

This color change in solutions of chromic salts is being further investigated experimentally in this laboratory, particularly as regards its velocity and the location of its equilibrium.

## THE TECHNICAL ESTIMATION OF ANTIMONY AND ARSENIC IN ORES, ETC.

By A. H. Low.

Received October 7, 1906.

THE technical estimation of antimony in ores containing also arsenic and possibly tin is frequently a tedious and more or less unsatisfactory operation. Distillation methods may give correct results, but considerable experience in their manipulation is usually required, and perhaps, also, special apparatus not always at the disposal of the technical chemist having only an occasional antimony determination to make. The following method for both antimony and arsenic is free from these objections, and,

<sup>1</sup> Recoura: Loc. cit.

<sup>2</sup> Pfeiffer: Loc. cit.

in my laboratory, has given results closely checking those obtained by distillation. While it is largely based upon old ideas there are some points of novelty that tend to expedite the work, and the method as a whole is different from any I have seen published. The time required for determining both antimony and arsenic in an ore need not exceed two and one-half hours.

Take 1 gram of the ore in a 150 cc. flask, add 7 grams of potassium acid sulphate, 0.5 gram of tartaric acid and 10 cc. of strong sulphuric acid. Heat over a free flame (manipulating the flask in a holder), cautiously at first, finally with the full power of a Bunsen burner, until any free sulphur is entirely expelled and the separated carbon is completely oxidized, leaving a clean mass or melt with but little free sulphuric acid. Allow to cool with the flask on its side, as otherwise the solidifying cake may break it, or, spread the melt around on the sides while cooling. The object of the tartaric acid in the decomposition is to reduce the arsenic and antimony to the *ous* condition, thus rendering the subsequent solution of the antimony easy and the precipitation of both metals as sulphides rapid and complete. A covered casserole may be employed instead of a flask, if considered more convenient.

After cooling, add 50 cc. of water, 10 cc. of strong hydrochloric acid and 2 or 3 grams of tartaric acid. Heat nearly to boiling for a short time to dissolve everything soluble (especially anhydrous iron sulphate), but do not actually boil for fear of volatilizing some arsenic. Filter, washing with hot water. This filtration is advisable but not a necessity. Dilute the filtrate to about 300 cc. with hot water, maintain the liquid warm and pass in hydrogen sulphide. The arsenic and antimony, being in the *ous* condition, are quickly precipitated, ten minutes being usually sufficient. Filter, washing with hydrogen sulphide water. Rinse the sulphides into a beaker with hot water, using as little as will suffice, add a little colorless potassium sulphide<sup>1</sup> and warm to extract the arsenic and antimony sulphides (also tin sulphide, if present). Pour through the last filter and wash with warm water containing a little colorless potassium sulphide. With small amounts of other sulphides present one extraction will usually suffice. Receive the filtrate in a 300 cc. flask. Add to it about 3 grams of potassium acid sulphate and 10 cc. of strong sulphuric

<sup>1</sup> If sodium sulphide is used a separation of sodium chloride crystals, occluding a little antimony, may occur later.

acid and boil the mixture, finally over a free flame, until the free sulphur is all expelled and the greater part of the free acid also. Allow the clear melt to cool with the flask on its side. When sufficiently cool add 25 cc. of water and 10 cc. of strong hydrochloric acid and warm to effect complete solution, then cool nearly to room temperature under the tap. Now add 40 cc. of strong hydrochloric acid and pass in hydrogen sulphide. The arsenic will be quickly precipitated, being in the *ous* condition. Filter, washing flask and precipitate with a mixture of 2 volumes strong hydrochloric acid and 1 volume of water. Before filtering, moisten the filter with the acid mixture. A double filter supported by a platinum cone will not break under very gentle suction.

The arsenic is now all on the filter and the antimony (together with any tin) in the filtrate. Determine the two metals as follows:

*Antimony.*—Dilute the filtrate with double its volume of warm water and pass in hydrogen sulphide. Filter the antimony sulphide and wash with hydrogen sulphide water sufficiently to remove most of the hydrochloric acid. Rinse the sulphide from the filter into a beaker, add a little ammonium sulphide and warm to effect solution. Pour through the last filter and wash with water containing a little ammonium sulphide. Receive the filtrate in a 300 cc. flask. Small amounts of antimony sulphide may be dissolved directly on the filter. To the filtrate add about 3 to 4 grams of (pure) potassium acid sulphate and 10 cc. of strong sulphuric acid. Boil as previously described to expel, first the water, then all the free sulphur and finally most of the free acid. Cool, add 50 cc. of water and 10 cc. of strong hydrochloric acid. Heat to effect solution and then boil for a few minutes to expel any possible sulphur dioxide. Finally, add 10 cc. more of strong hydrochloric acid, cool under the tap, dilute to about 200 cc. with cold water and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. Tin, if present, exists as stannic sulphate and is without influence. The oxalic acid value of the permanganate multiplied by 0.9532 will give the antimony value.

*Arsenic.*—Thoroughly wash out the hydrochloric acid from the sulphide with hydrogen sulphide water, also rinsing out any sulphide remaining in the flask. Dissolve the sulphide (this may usually be done on the filter) in warm ammonium sulphide solution and wash with the same solution diluted. Receive the

filtrate in a 300 cc. flask. Add 2 to 3 grams of potassium acid sulphate and 5 cc. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 cc. of water and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator and then add ammonia until the solution is slightly alkaline. Again acidify slightly with hydrochloric acid and cool to room temperature. Finally add 3 to 4 grams of sodium acid carbonate and a little starch liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue color.

The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide and diluting to 1 liter. Standardize with arsenious oxide. Dissolve about 0.150 gram in 5 cc. of strong hydrochloric acid by warming very gently, dilute and neutralize as described above and finally titrate with the iodine solution. One cc. of the latter will equal about 0.003 gram of arsenic.

It is perhaps unnecessary to enumerate a long list of instances showing the accuracy of the above method and I will therefore mention only the following:

	Taken Gram.	Found. Gram.
As.....	0.0792	0.0798
Sb.....	0.0534	0.0531
Sb.....	0.0516	0.0514
Sb.....	0.0521	0.0525

With an oxidized ore: As, 0.568 per cent.; Sb, 0.106 per cent.  
Repeat: Sb, 0.106 per cent.

On this ore Pearce's method (modified) gave As, 0.57 per cent.

The same ore gave, by Knorr's distillation method, Sb, 0.082 per cent.

Ledoux & Co., of New York, reported Sb, 0.081 per cent.

Mr. R. L. Wilder, of El Paso, tested this ore by the new method and found Sb, 0.1005 and 0.0802 per cent.

## SEASONAL VARIATIONS IN THE COMPOSITION OF COWS' MILK.

BY H. C. SHERMAN.

Received September 24, 1906.

It is well-known that cows' milk tends to show higher percentages both of fat and of solids-not-fat in winter than in summer, and the extent of these variations as shown by the average composition of many thousands of samples received by the Aylesbury Dairy Company of London has been determined by Richmond for several years past.<sup>1</sup> Comparatively few data are available to show whether the seasonal variations found in England apply likewise to American conditions, or to determine to which constituent the variation in percentage of solids-not-fat is chiefly due.<sup>2</sup>

The average results of a series of analyses covering five years and bearing upon these points is shown below, Table I. The figures given for each month are obtained by averaging the results of analyses of monthly samples of the mixed milk of the herd, taken at the afternoon milking of one day each month for five successive years. The results as a whole represent complete analyses of 60 samples, each an accurate composite of the entire milk of a dairy herd in Westchester County, New York, averaging about 600 cows. About one-third of the cows were registered Jerseys and most of the remainder were Jersey grades. Before and during the time covered by this investigation the cows were selected and the herd managed with a view to the production of milk rich in fat. The system of feeding was liberal throughout. During the first two years, hay, grain and pasture were used exclusively; later, roots and ensilage were sometimes added to the ration. The herd was warmly housed in winter and was so managed that the proportion of fresh cows did not differ greatly at different seasons of the year. It is believed, therefore, that the differences shown by the average results for each month may

<sup>1</sup> Dairy Chemistry (London, 1899) and yearly papers in *The Analyst*.

<sup>2</sup> A series of analyses covering two years and bearing upon the same question has been published in a previous paper from this laboratory. *This Journal*, 25, 132 (1903).

properly be attributed to seasonal variations in the composition of the milk.

The results of the analyses covering September, 1900, to August, 1905, inclusive, are shown in Table I.

TABLE I.

Average Composition of Afternoon Milk, September, 1900, to August, 1905.

	Fat.	Solids-not-fat	Protein	Milk-sugar.	Ash.	Total solids.
January, average.....	5.57	9.37	3.80	4.82	0.76	14.94
February, " .....	5.52	9.39	3.77	4.86	0.76	14.91
March, " .....	5.46	9.27	3.66	4.86	0.75	14.73
April, " .....	5.42	9.18	3.60	4.84	0.74	14.60
May, " .....	5.40	9.17	3.57	4.86	0.74	14.57
June, " .....	5.53	9.11	3.57	4.79	0.75	14.64
July, " .....	5.24	8.96	3.49	4.73	0.74	14.20
August, " .....	5.26	9.02	3.53	4.74	0.74	14.28
September, " .....	5.33	9.15	3.62	4.79	0.74	14.48
October, " .....	5.36	9.26	3.70	4.81	0.75	14.62
November, " .....	5.38	9.35	3.80	4.81	0.75	14.73
December, " .....	5.52	9.43	3.85	4.82	0.76	14.95
General " .....	5.42	9.22	3.66	4.81	0.75	14.64

The average results for the five-year period indicate that the percentages of fat, protein and milk-sugar (and of total solids and solids-not-fat) all reach a minimum in July, while the maximum percentages are reached in December, January or February.

The average results for the fat and solids-not-fat as given by Richmond for the afternoon milk of the same five years<sup>1</sup> have been calculated by months with the results shown in Table II.

Comparison of Richmond's results with those of the writer shows that the minimum percentages are reached at about the same time, usually in July. In the following months the solids-not-fat rise steadily in both cases and are highest in December, January and February, while the percentage of fat rises more rapidly in the English than in the American samples, being highest in October and November in the former, and in January in the latter. The highest average percentages of total solids are found in October, November and December by the English, and in December, January and February by the American analyses.

<sup>1</sup> The mean monthly averages found by Richmond for a period of sixteen years ending 1899 are given in his *Dairy Chemistry*, p. 127, and show variations similar to those in Table II, except that the maximum for solids-not-fat occurs somewhat earlier in the older series of analyses.



TABLE II.

Average Results of Richmond's Analyses, September, 1900, to August, 1905, Inclusive.

	Fat.	Solids-not-fat.	Total solids.
January, average.....	3.99	9.02	13.01
February, " .....	3.92	9.00	12.92
March, " .....	3.89	8.98	12.87
April, " .....	3.86	8.93	12.79
May, " .....	3.85	8.97	12.82
June, " .....	3.79	8.92	12.71
July, " .....	3.82	8.77	12.59
August, " .....	3.99	8.78	12.77
September, " .....	4.04	8.88	12.92
October, " .....	4.14	8.94	13.08
November, " .....	4.14	8.96	13.10
December, " .....	4.10	8.98	13.08
General " .....	3.96	8.93	12.89

In order to bring the results into form convenient for comparison the average figure for each month for fat, solids-not-fat, and total solids is calculated as percentage of the general average and these percentages for Richmond's analyses and those of the writer are given in Table III.

TABLE III.

Monthly Averages in Percentages of General Averages: Fat, Solids-not-fat, and Total Solids.

	Fat.		Solids-not-fat.		Total solids.	
	Richmond, London.	Sherman, New York.	Richmond, London.	Sherman, New York.	Richmond, London.	Sherman, New York.
January .....	100.8	102.8	101.0	101.6	100.9	102.0
February ...	99.0	101.8	100.8	101.8	100.2	101.8
March .....	98.2	100.7	100.6	100.5	99.8	100.6
April .....	97.5	100.0	100.0	99.6	99.2	99.7
May .....	97.2	99.6	100.4	99.5	99.5	99.5
June .....	95.7	102.0	99.9	98.8	98.6	100.0
July .....	96.5	96.7	98.2	97.2	97.7	97.0
August .....	100.8	97.0	98.3	97.8	99.1	97.5
September...	102.0	98.3	99.4	99.2	100.2	98.9
October .....	104.5	98.9	100.1	100.4	101.5	99.9
November ..	104.5	99.3	100.3	101.4	101.6	100.6
December ...	103.5	101.8	100.5	102.3	101.5	102.1

The results of a similar calculation of the percentage variation of the monthly averages for protein, milk-sugar, and ash in the samples of New York milk are shown in Table IV.

TABLE IV.

Monthly Averages in Percentage of General Averages: Protein, Milk-sugar and Ash.

	Protein.	Milk-sugar.	Ash.
January.....	103.8	100.2	101.3
February.....	103.0	101.0	101.3
March.....	100.0	101.0	100.0
April.....	98.1	100.6	98.7
May.....	97.3	101.0	98.7
June.....	97.3	99.6	100.0
July.....	95.4	98.3	98.7
August.....	96.4	98.5	98.7
September.....	99.5	99.6	98.7
October.....	100.5	100.0	100.0
November.....	103.8	100.0	100.0
December.....	105.2	100.2	101.3

The variations of individual constituents in the New York samples are compared in Table V both for single months and for six-month periods.

TABLE V.

Comparison of Seasonal Variations: Fat, Protein, Sugar and Ash.

	Fat.		Protein.		Milk-sugar.		Ash.	
	Average per cent. in sample.	Per cent. of general average.	Average per cent. in sample.	Per cent. of general average.	Average per cent. in sample.	Per cent. of general average.	Average per cent. in sample.	Per cent. of general average.
Max. monthly average...	5.57	102.8	3.85	105.2	4.86	101.0	0.76	101.3
Min. monthly average..	5.24	96.7	3.49	95.4	4.73	98.3	0.74	98.7
Difference.....	0.33	6.1	0.36	9.8	0.13	2.7	0.02	2.6
Aver. October to March..	5.47	100.9	3.76	102.6	4.83	100.4	0.755	100.7
Aver. April to September	5.36	98.9	3.57	97.3	4.79	99.6	0.742	98.9
Difference.....	0.11	2.0	0.19	5.3	0.04	0.8	0.013	1.8

## CONCLUSIONS.

Monthly analyses of the mixed milk of about 600 cows extending over a period of five years show seasonal variations in percentages of fat and solids-not-fat similar in general to those found by Richmond but differing in that the fat varied less in proportion to the amount present and reached a maximum somewhat later in the winter, while the solids-not-fat varied more than in Richmond's samples for the same period, and reached a maximum about a month earlier.

The seasonal variation was more regular, and was greater both in actual figures and in proportion to the amount present, in the case of protein than in the case of fat.

From October to March the average percentages of all the constituents were higher than from April to September. The difference in milk-sugar is much less, both relatively and absolutely, than the differences in protein and fat. The seasonal variation in percentage of ash is very slight, although in proportion to the amount present it is no smaller than the variation in milk-sugar.

The seasonal variations in solids-not-fat are due chiefly to changes in the percentage of protein.

## THE DETERMINATION OF ROSIN IN VARNISHES.

BY AUGUSTUS H. GILL.

Received October 1, 1906.

THE presence of rosin in a varnish decreases its resisting power to atmospheric agencies, its power of adhesion to surfaces, and its hardness; furthermore, it means the substitution of the valuable copal or kauri by the cheap rosin or "South Carolina Zanzibar."

The procedure followed consists in the elimination of the turpentine by distillation with steam, of the oil by Twitchell's process, thus obtaining the pure gum resins. These were examined at first by the Hubl method, Table I, then by McIlhiney's bromine method, Table II, and finally and most satisfactorily, the saponification, free acid and ester values, Table V, were determined.

Sixty grams of the well-mixed varnish are weighed into a 500 cc. round-bottomed flask, this connected with a condenser and a two-quart can which furnishes steam; the varnish is warmed just above 100° by a small flame and kept at this point to prevent the condensation of the steam used for distillation. The distillation is continued until about 500 cc. of water have passed over, or until there is but a faint odor of turpentine in the last portions of the distillate. It was noticed with a pure rosin varnish that only a small portion of the gum sticks to the flask, while with pure copal varnish the gum coats the inside of the flask almost completely.

The solvent may be separated from the water, dried by anhy-

drous sodium sulphate, distilled and weighed; if the specific gravity be taken, a fairly good idea of its purity may be obtained.

The residue in the flask is boiled for an hour over a free flame at a reflux condenser with 150 cc. of normal alcoholic potash; this latter is made from absolute alcohol and "potash purified by alcohol." Care should be taken to warm the flask very slowly or on a water-bath first, to prevent the usual bumping of alcoholic solutions; the solution is then cooled, separated from the residue and the latter again treated with the potash solution, repeating the process until practically complete saponification takes place. Usually a residue of about 1 per cent. remains.

The solutions are united in a separatory funnel and neutralized with hydrochloric acid, causing a precipitate of potassium and lead chlorides, the latter coming from the drier used; water and ether are now added, the latter dissolving the fatty acids and gums liberated by the acid. The ethereal solution is run into a flask, the ether distilled off and a small quantity of absolute alcohol added to the contents of the flask; on this being heated the alcohol passes off carrying the water with it, leaving the dry gums and fatty acids. These are dissolved in 10 volumes of absolute alcohol, any residue being added to the gums obtained below, from carrying out this process. Dry hydrochloric acid gas is passed into this solution, it being cooled by ice, until it is saturated. Hot water is poured into the flask and its contents boiled over a free flame, care being taken at incipient ebullition to prevent frothing over.

The contents of the flask are cooled and shaken out with ether, which dissolves the gums and gum acids, dilute alcoholic potash (2.5 grams potassium hydroxide, 200 cc. water, 20 cc. alcohol) is added to the ether solution and the shaking continued. This dissolves the gum acids which together with any gums are drawn off, leaving the esters of the linseed oil acids in the ethereal layer. The resin soap solution is acidified, the acids dissolved in ether, the residue insoluble in alcohol, mentioned above, added to the solution and the whole evaporated in a small beaker on the water-bath. A small quantity of absolute alcohol is added and the evaporation repeated. This removes any water; portions of the material in the beaker are chipped out, dried over sulphuric acid and their iodine and bromine numbers determined.

From the results given by different observers it was thought

that the Hübl iodine value could be used as a means of discrimination between a pure varnish gum and one adulterated with rosin. The iodine figures given by Schmidt and Erban<sup>1</sup> are as follows: Rosin 11.7, Angola copal, melted 42. Williams gives rosin 112, copal 130-138. Accordingly, the iodine number was determined in the usual way using Hübl's procedure, by solution in chloroform and, except in the case of samples A and B, the iodine was allowed to act for four hours; in these cases it acted for twenty-four.

In handling these recovered gums it is well to bear in mind that they cannot be kept much longer than one month without hardening to such an extent as to be insoluble in chloroform and carbon tetrachloride.

TABLE I.—IODINE NUMBERS OF GUMS OBTAINED FROM VARIOUS VARNISHES.

Sample.	Composition.	Maker.	Iodine numbers.	
A	Quick rubbing varnish—pure kauri.....	B. Co.	64.1	68.2
B	Quick rubbing varnish—pure kauri.....	B. Co.	68.6	59.3
C	Elastic rubbing varnish—pure kauri.....	B. Co.	46.4	47.1
D	Elastic rubbing varnish—pure kauri.....	B. Co.	48.9	47.5
E	Pure rosin varnish.....	G. Co.	68.2	69.4
F	Pure rosin varnish.....	G. Co.	64.4	64.3
G	Half rosin and half kauri varnish.....	G. Co.	67.5	69.3
H	One-fourth rosin and three-fourths kauri varnish.....	G. Co.	62.2	62.5

Samples A and B, C and D, E and F were the same varnishes but worked through separately.

By comparing Sample E, pure rosin, with Sample G, which is half rosin and half kauri, practically no difference is seen in the iodine numbers, hence these cannot be used as criteria by which to judge of the purity of a varnish.

The iodine value being of so little use, it was hoped that the process devised by McIlhiney would give results of more value. The method as given by him<sup>2</sup> was applied to the gums extracted as detailed previously with the results in Table II.

The last eight results were obtained by a different operator carrying through the method at two different times.

The results do not agree remarkably well, although certain results, particularly with the pure rosin E and the one-fourth rosin varnishes H, are as close as they can be expected. The

<sup>1</sup> Dieterich: Die Hürze.

<sup>2</sup> This Journal, 21, 1084.

difficulty seems to be due to the emulsification of the carbon tetrachloride with the potassium iodide, which masks the end-point. The tendency to emulsification seems to be less with a pure rosin than with a kauri varnish.

TABLE II.—BROMINE NUMBERS OF VARIOUS GUMS OBTAINED FROM VARNISHES.

Sample.	Composition.	Addition.	Substitution.	Total.
A	Pure kauri.....	54.3	26.3	106.9
A	Pure kauri.....	60.5	26.0	112.4
B	Pure kauri.....	57.5	23.6	104.7
C	Pure kauri.....	75.5	3.3	82.1
C	Pure kauri.....	76.6	4.7	86.0
E	Pure rosin .....	10.9	45.2	101.4
E	Pure rosin .....	9.9	44.7	99.9
G	Half rosin and half kauri.....	21.2	54.2	129.6
	Half rosin and half kauri.....	12.2	47.9	108.1
H	One-fourth rosin and three-fourths kauri.....	44.9	36.5	111.9
	One-fourth rosin and three-fourths kauri.....	50.9	35.8	122.0
E	Pure rosin ....	5.9	45.4	96.7
		0.4	50.1	100.6
		6.0	54.2	114.4
		1.1	58.1	117.3
H	One-fourth rosin and three-fourths kauri.....	45.2	34.4	114.0
		51.0	31.5	114.0
		37.2	35.1	107.4
		42.0	33.5	109.0

Notwithstanding this disagreement, it is easy to determine from the substitution values in the table which varnishes contain rosin, being evidently E, G and H. There is so much irregularity in the numbers obtained that the method would not seem to be a satisfactory quantitative one.

The method was modified as follows: Such quantities of the resin were employed so that if 20 cc. of N/3 bromine solution were used, the amount of bromine left after a certain time had elapsed was very nearly equal to the amount which had acted upon the resin. The time of action of the bromine was three minutes. From 0.4 to 0.5 gram of resin was weighed into a 50 cc. graduated flask, dissolved in carbon tetrachloride and brought to the mark with the same; 10 cc. of this solution were used for each determination. Window glass and black rosin were used to familiarize the operator with the method; in some cases an insoluble residue

remained after treatment with the solvent—the clear liquid only was employed. It was found, however, that there was no difference as to whether this or the turbid liquor were used.

Table III shows a comparison of McIlhiney's original method and this modification; window glass rosin was used.

TABLE III.—BROMINE NUMBERS OF ROSIN BY VARIOUS METHODS.

Total.	Added.	Substituted	
125.5	23.3	51.1	} original.
119.3	14.6	52.3	
102.8	24.4	39.2	} clear solution.
103.0	23.8	39.6	
102.3	22.7	39.8	} modified turbid solution.
101.8	25.5	38.1	

The method as modified was applied to resins from varnishes B, F and H from Table II and also to a suspected varnish I.

TABLE IV.—BROMINE NUMBERS OF VARIOUS GUMS.

Sample.	Composition.	Total.		Bromine added.		Substituted.
B	Pure kauri.....	108.7	107.7	70.1	73.8	19.3 17.0
F	Pure rosin.....	80.4	84.4	1.6	3.1	39.4 40.6
H	$\frac{1}{4}$ R $\frac{3}{4}$ K.....	91.4	84.4	34.5	28.6	28.5 22.9
I	Unknown.....	76.4	76.4	45.3	41.9	15.5 17.3

Sample I is evidently not adulterated with rosin, as was shown by other tests.

The results from the Hübl and the McIlhiney processes being so unsatisfactory from a quantitative point of view, the saponification, free acid and ester values of these various gums were now obtained. These were determined in the usual way, as described in the writer's "Handbook of Oil Analysis;" the ester value is, of course, the difference between the two.

TABLE V.—SAPONIFICATION, FREE ACID AND ESTER VALUES OF GUMS FROM VARIOUS VARNISHES.

Sample.	Composition.	Maker.	Saponi- fication.	Free acid.	Ester	Average.
E	Pure rosin, No. 1.....	G. Co.	182.3	160.1	22.2	23.1
	Pure rosin, No. 6.....	G. Co.	185.7	161.7	24.0	
	Ordinary rosin not run		172.3	159.7	12.6	
H	One-fourth rosin, three- fourths kauri, No. 5..	G. Co.	134.8	62.0	72.8	75.3
	One-fourth rosin, three- fourths kauri, No. 7..	G. Co.	121.6	43.9	77.7	
	Half rosin and half kauri, No. 3.....	G. Co.	143.5	88.0	55.5	
G	Kauri gum.....		124.2	41.0	83.2	84.0
	Kauri, No. 2.....		129.7	45.0	84.7	

Using the average ester values obtained and the usual formula  $x = \frac{100(1-n)}{m-n}$  for calculating the percentage of adulteration, we find that the three-quarters kauri varnish figures 85 per cent., and the half and half kauri and rosin 53 per cent. It would seem that this method is fairly satisfactory but requires experimentation by other observers before implicit trust can be placed in it.

In conclusion, the writer wishes to express his indebtedness to his various assistants and students, Messrs. Hammond, Sulzer, Tufts, Merrill and Mason.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
September, 1906.

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## THE TECHNICAL DETERMINATION OF BENZENE IN ILLUMINATING GAS.<sup>1</sup>

BY D. A. MORTON

Received September 26, 1906.

THE value of benzene vapor as a light producer in illuminating gas has led to its extensive use for enriching purposes, and its exact estimation in a simple way has become a matter of consequence.

Since 1 per cent. only in coke oven gas gives a lighting value of more than twelve candle-power, while 1 per cent. of ethylene gives less than one and one-half candle-power, there is a large difference in the lighting value of these constituents and their separate determination is necessary.

Although a number of methods have been proposed for the determination of benzene and some of these requiring long and careful manipulation are quite exact, none appears to be satisfactory for use in technical work where a simple and rapid, as well as reasonably accurate, test is desired.

W. Misteli,<sup>2</sup> in a recent review, cites the method of Haber and Oechelhaeuser<sup>3</sup> as being the only one suitable for testing small quantities of gas, yet even this method does not compare in rapidity and simplicity with the ordinary volumetric tests in technical analyses. The gist of the method is the absorption of the ethylene by bromine water and subsequent titration of the

<sup>1</sup> Read at the Ithaca Meeting of the American Chemical Society.

<sup>2</sup> J. Gasbeleucht, Sept. 9, 1905, p. 804.

<sup>3</sup> Ber. 29, 2700.



excess of bromine. Benzene vapors, the authors claim, while dissolving completely or partially in the bromine water, do not unite chemically with the bromine and hence do not affect the titration. Only by long contact is there a slight reaction with the benzene. The difference between the ethylene found and the total illuminants is taken as the percentage of benzene.

The method of Dennis and O'Neill,<sup>1</sup> published in 1903, in which the benzene vapors are absorbed by shaking the gas in a pipette with ammonium nickel nitrate solution of prescribed strength, is, unlike the preceding method, simple and rapid and suitable in these respects for technical use. The nickel method was used for a considerable time in this laboratory because, on account of its convenience and supposed accuracy, it was presumed to be suitable for the purposes here required. Nevertheless on a number of occasions the tests were found to be incorrect and consequently a more exhaustive investigation of its merits was finally carried out, with results of such interest that we give them in detail below.

#### INVESTIGATION OF THE AMMONIUM NICKEL NITRATE METHOD.

The ammonium nickel nitrate solutions for the experiments were made up according to the directions given in the original article.<sup>2</sup> Both the regular solution and Geer's solution were tried, with identical results; and, since the solutions were made up by more than one analyst and at a number of different times, we cannot suppose the errors found in the tests to have been due to errors in preparing the solutions.

Following the directions of the authors in carrying out the tests, mixtures of benzene vapor and air were analyzed, 100 cc. of the gas mixture being shaken three minutes in an absorption pipette with the ammonium nickel nitrate solution, then three minutes in a second pipette with 5 cc. of 5 per cent. sulphuric acid over mercury to remove ammonia fumes. The decrease in volume by this treatment indicates the percentage of benzene.

Table "A" shows the results obtained. The percentage of benzene present in each case was determined by absorption with fuming sulphuric acid as in the regular way for illuminants. Besides the percentage of benzene present, and that found by the ammonium nickel nitrate test, the table gives the cubic centimeters

<sup>1</sup> This Journal, 25, 503 (1903).

<sup>2</sup> Loc. cit., p. 505.

of benzene vapor previously absorbed by the reagent, for this has a decided influence, as will appear.

TABLE "A."

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Per cent. benzene present..	0.0	0.5	0.6	0.6	4.3	4.7	0.5	1.0	1.8	4.2
Per cent. benzene found...	—1.1	0.0	0.1	0.3	3.3	3.2	0.35	0.7	1.4	3.7
Benzene vapor previously absorbed, cc.....	17.	17.	17.	1.	8.	12.	0.	0.	0.	0.

A glance at these results shows that the absorbing solutions must be perfectly fresh to obtain results that are even approximately correct. In tests 2 to 6, although at most only a small quantity of benzene vapor had previously been absorbed, in no case has more than three-fourths the benzene actually present been found by the test. In 1, 100 cc. of air, shaken with the reagent and the 5 per cent. sulphuric acid, has its volume *increased* to 101.1 cc.

If fresh ammonium nickel nitrate solution and fresh 5 per cent. sulphuric acid are used for each test (7 to 10) the results are better, though still too low by several tenths of 1 per cent. In technical works where complete analyses have sometimes to be made as frequently as once an hour, refilling the pipettes with fresh solutions for every test is an inconvenience that is best avoided. An improvement has been made in the laboratory of the Detroit Solvay works where the gas mixture is shaken three minutes in each of two ammonium nickel nitrate pipettes, thus keeping the contents of the second pipette comparatively fresh for some time.

On further examination we find not only that the ammonium nickel nitrate solution is an indifferent absorbent for benzene, but also that the absorbing power it does possess is due, *not to the nickel compound but to the water present*. That either water alone or dilute aqua ammonia gives practically the same results as the ammonium nickel nitrate solution is shown in the table of comparative tests given below.

Table "B" shows results from a number of tests made under conditions as nearly identical as possible in all comparative cases. In "1" fresh absorbing solutions were used. The gas taken for the test was air containing benzene vapor. One hundred cc. of the gas were passed into the absorbing pipette and shaken with the absorbent for the number of minutes indicated, drawn out and passed into a pipette of 5 per cent. sulphuric acid to remove

fumes, then back into the burette, allowed the usual time to drain, and measured. In "II" the same conditions were observed except that the absorbing solutions were not fresh, having been used for the tests under "I." In "III" the gas in each case was shaken with the fresh reagent three minutes, then with 5 per cent. sulphuric acid three minutes, the tests all being made with especial care.

Table "C" shows the results of strictly comparative tests of the absorbing power of ammonium nickel nitrate solutions and pure water. In each case exactly 118 cc. of the absorbing solution were shaken for the time stated with 100 cc. of the gas and the unabsorbed residue drawn slowly back into the burette and measured. The gas was drawn back slowly to insure complete absorption of all ammonia fumes. (One hundred cc. of air passed into the fresh ammonium nickel nitrate solution, shaken one minute and drawn back in the same way remeasured exactly 100 cc.) Temperatures were the same, 18-19°, in all instances. In each case the gas tested was a mixture of air and a known quantity of benzene vapor.

TABLE "B."

"I."			
Absorbing solution.	Am. Ni nitrate.	Aqua ammonia (Sp. gr. 0.95).	Water.
Minutes shaken .....	3	2	3
Per cent. benzene present .....	9.9	9.9	9.5
Per cent. benzene found.....	9.0	8.8	8.1
Benzene vapor previously absorbed.....	0	0	0

"II."

Minutes shaken .....	3	3	3
Per cent. benzene present.....	9.9	9.9	8.4
Per cent. benzene found.....	8.0	8.2	7.4
Benzene vapor previously absorbed, cc.	9.0	8.8	8.1

"III."

Number of test.	1.	2.	3.	4.	5.	6.
Per cent. benzene present .....	0.5	1.0	1.8	4.15	3.95	4.15
Per cent. benzene by Am. Ni. nitrate.....	0.35	0.7	1.4	3.65	.....	3.6
Per cent. benzene by water.....	0.4	0.8	1.5	3.4	3.5	3.35

TABLE "C."

Series.	Absorbing solution.	Minutes shaken.	Per cent. benzene found.	Per cent. benzene present.	Cc. benzene previously absorbed.
I.	Am. Ni. nitrate .....	2	6.2	7.2	0
	Water.....	2	6.0	7.2	0
II.	Am. Ni. nitrate .....	3	2.3	3.6	6
	Water.....	3	2.3	3.6	6
III.	Am. Ni. nitrate .....	2	0.4	1.0	0
	Water.....	2	0.4	1.0	0

From the above results we can draw no other conclusion than that in the determination by ammonium nickel nitrate solution, the benzene vapor is simply dissolved to a certain extent by the water in the solution—perhaps increased slightly by the ammonia in the case of the high percentages—but that the presence of the nickel compound has no appreciable influence whatever.

It would answer better to simply use fresh water each time as the solution for absorbing benzene and, if used under proper conditions, good results could perhaps be obtained with this reagent. Nevertheless the use of a fresh solution, even water, for every test involves certain inconveniences and liabilities to error and would be objectionable in technical practice.

By the use of concentrated sulphuric acid for the benzene absorption a better method is obtained. This method is reliable and convenient, and the results by it are so comparatively accurate that we have no hesitation in recommending it for the technical analysis of coal gases.

#### THE CONCENTRATED SULPHURIC ACID METHOD.

The marked solubility of benzene vapor in water (see Tables "B" and "C" above) renders necessary certain precautions in sampling and handling the gas previous to the test. If taken over water, the sample bottle should be completely filled with the gas, driving out practically all of the water, as otherwise some of the benzene will be absorbed.

After the determination of the carbon dioxide in the gas, by absorption in strong caustic soda<sup>1</sup> or potash solution in the usual manner, the benzene test is accomplished as follows:

The gas residue is passed into an ordinary simple absorption pipette containing concentrated sulphuric acid (sp. gr. 1.84)<sup>2</sup> and shaken *vigorously* with this reagent for one minute, by which treatment the benzene vapors are absorbed. The shaking is satisfactorily accomplished by giving a quick sharp motion to the pipette in such a way as to mix the contents thoroughly about twice per second, during the specified one minute. It is essential to shake vigorously with the sulphuric acid as directed, for the last traces of benzene are absorbed slowly and require thorough contact with the acid.

<sup>1</sup> Caustic soda solution dissolves benzene to only a very slight extent, and the error caused thereby is negligible.

<sup>2</sup> Slight dilution of this acid does not detract from its efficiency, but the dilution should not exceed 2 per cent.

Experimental data on the conduct of concentrated sulphuric acid as an absorbent for benzene are given in the tables below.

Table "D" shows results obtained with mixtures of benzene and air. Good results are obtained even when more than 7 per cent. of benzene—a very high amount—is present.

Table "E" gives results showing that the concentrated sulphuric acid can be used for a large number of tests without renewal. The benzene combines with the sulphuric acid and is not removed by air subsequently introduced.

Table "F" shows the action of concentrated sulphuric acid on benzene-ethylene-air mixtures. The benzene is determined by the concentrated sulphuric acid test; the ethylene immediately afterward by fuming sulphuric acid in the usual way. In this table a slight defect in the method appears, due to the absorption of a trace of ethylene by the concentrated sulphuric acid. Higher homologues of ethylene would be absorbed to a greater extent than ethylene itself. The error diminishes rapidly as the percentage of benzene increases, becoming practically nil when 1 per cent. or more of the latter is present and probably not exceeding 0.2 per cent. in the case of any coal gas.

Table "G" shows the cubic centimeters of ethylene absorbed by the concentrated sulphuric acid test, per 100 cc. of gas, having given the percentage of benzene and ethylene present. By use of these data correction for the error can be made when desirable.

TABLE "D."

## Benzene-Air Mixtures.

Number of test	1	2.	3.	4.	5.	6	7.	8.	9.	10.
Per cent. benzene present...	0.5	0.6	0.65	1.9	3.0	3.6	4.0	4.5	4.7	7.8
Per cent. benzene found.....	0.5	0.6	0.6	1.9	3.1	3.55	3.8	4.35	4.6	7.7

TABLE "E."

## Benzene-Air Mixtures.

Gas tested Number of test.	Benzene-air. 1.	Benzene-air 2.	Benzene-air. 3.	Air. 4.	Air. 5.
Benzene vapor previously absorbed, cc.....	55.	120.	150.	55.	100.
Per cent. benzene present.....	1.9	3.0	4.5	0.0	0.0
Per cent. benzene found.....	1.9	3.1	4.3	0.0	0.0

TABLE "F."

## Benzene-Ethylene-Air Mixture.

Number of test.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Per cent. benzene present..	0.55	0.50	0.50	0.50	1.0	1.0	1.0	2.85	3.0
Per cent. benzene found.....	0.85	0.70	0.65	0.60	1.05	1.0	1.05	2.85	3.0
Per cent. ethylene present.	9.5	10.1	4.8	5.0	9.95	4.8	5.0	4.4	4.5
Per cent. ethylene found....	9.5	10.0	4.7	4.8	10.1	4.8	5.0	4.6	4.7

TABLE "G."

Cubic Centimeters Ethylene Absorbed in Benzene Test.

	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Ethylene present.....	1.0	2.0	3.0	4.0	5.0	6.0
Per cent.	cc.	cc.	cc.	cc.	cc.	cc.
Benzene present.....	0.0	0.05	0.10	0.15	0.20	0.25
Benzene present.....	0.5	0.00	0.05	0.05	0.10	0.15
Benzene present.....	1.0	0.00	0.00	0.00	0.05	0.10

## CONCLUSIONS.

From the results obtained the unsatisfactory character of the ammonium nickel nitrate method is apparent. As pure water absorbs benzene to practically the same extent as the ammonium nickel nitrate solution, it appears that the method really depends on the solubility of benzene vapor in water, or ammoniated water, and that the presence of the nickel compound has no influence. The results by the method are inaccurate and vary widely according to the amount of benzene in the gas and the quantity already present in the absorbing solution.

Concentrated sulphuric acid, on the other hand, absorbs benzene vapor as readily as could be desired, and can be used for a large number of tests without renewal, giving as accurate results after a hundred tests as when first prepared. The defect due to the absorption of ethylene is insignificant but may be easily corrected for (see Table "G"). Traces of the higher olefines, however, may give a value slightly too high for the benzene percentage, though this error, as shown by our tests of rich and lean gases from a variety of coals, must be small, if not inappreciable.

LABORATORY OF THE SOLVAY PROCESS CO.,  
SYRACUSE, N. Y., June, 1906.

## NOTE.

*Solubilities of Permanganates of the Alkali Metals.*—The article by Baxter, Boylston and Hubbard on "The Solubility of Potassium Permanganate,"<sup>1</sup> reminds the writer that in the course of some work on the preparation of various permanganates, at Johns Hopkins University in 1900, a few solubility determinations were made, the results of which have not been published except in his dissertation. They are reproduced below, together with some extracts from the dissertation. The permanganates of rubidium and caesium were made by neutralizing the pure

<sup>1</sup> This Journal, 28, 1336.

carbonates with electrolytically prepared permanganic acid (6 per cent. solution). All the salts were freed from manganese dioxide by filtering their solutions through asbestos.

At 0°	100 cc. solution contain 2.84 gram $\text{KMnO}_4$ .
" 15°	" " " " 5.22 " "
" 15.3°	" " " " 5.30 " "
" 30°	" " " " 8.69 " "
" 2°	" " " " 0.46 " $\text{RbMnO}_4$ .
" 19°	" " " " 1.06 " "
" 60°	" " " " 4.68 " "
" 1°	" " " " 0.097 " $\text{CsMnO}_4$ .
" 19°	" " " " 0.23 " "
" 59°	" " " " 1.25 " "


"In making the determinations, the following method was employed: A glass-stoppered bottle, containing water and a large excess of the recrystallized salt, was placed in water kept at a constant temperature. The bottle was allowed to remain in the bath for several hours, and was agitated thoroughly at short intervals. With a corrected thermometer the temperature of the saturated solution was determined and the latter was then drawn by suction through a glass tube containing a plug of asbestos. The first portions of the filtrate were discarded. The strength of the filtered solution was determined by titration against an accurately standardized solution of oxalic acid, a method whose error is smaller than that encountered in reading the thermometer. Care was taken to keep the temperature of the filtering apparatus the same as, or a little higher than that of the solution, in order to prevent any of the salt from crystallizing out.

"When saturated solutions of caesium permanganate at the boiling temperature are made, a little decomposition is observed, and more manganese dioxide is precipitated than when rubidium is subjected to the same treatment. On cooling, the flaky oxide is easily removed from the heavy, difficultly soluble salt by washing with cold water.

"To our best knowledge, only one previous determination for rubidium permanganate is on record, and not having been published in a chemical journal escaped our notice until after the curves were drawn. Muthmann and Kuntze<sup>1</sup> found at 7° in

<sup>1</sup> Z. Krystallogr. 23, 377.

100 cc. of solution 0.603 gram of the salt. This value falls on the curve given in the plate.

"We see then that in solubility the permanganates bear a general resemblance to the chlorplatينات in that those of most of the heavy metals are very soluble, while those of the alkali metals, and particularly of caesium dissolve in water with difficulty. The saturated solution of the latter at 0° is light violet in color, and even permits one to detect the presence in it of free acid with litmus paper. At the same temperature strontium permanganate is about 2,700 times, and calcium permanganate nearly 3,000 times, as soluble." 

The specific gravity of the saturated solution of potassium permanganate at 15° is 1.035; hence, according to the writer's determination above, 100 parts of water dissolve 5.31 grams at this temperature. This value confirms the accuracy of Baxter, Boylston and Hubbard's curve and shows that the widely recorded value of Mitscherlich is considerably too high.

AUSTIN M. PATTERSON.

SPRINGFIELD, MASS.,  
Oct. 4, 1906.

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## REVIEW.

### REVIEW OF ANALYTICAL WORK DONE ABROAD IN 1905.

BY BENTON DALES.

Received September 10, 1906.

IN THIS review the same general classification is used as in that of last year, and the articles are reviewed with the same purpose, namely, that an experienced chemist may be able to repeat the work. The effort is made to include a reference to the more important articles published; the review could not be made complete in reasonable space except it were a mere bibliography. The writer acknowledges his indebtedness to the *Chemisches Central-Blatt* for abstracts and for the general classification.

#### GENERAL ANALYSIS.

Büeler de Florin (*Chem. Ztg.* 29, 569) made some improvements upon Secchi's method of determining the transparency of liquids. The latter recommended sinking a white disk in the liquid till it was no longer visible to the observer's eye; the distance from liquid surface to disk he called the limit of visibility of the liquid. To avoid the effect of position of the sun, clouds, etc., Büeler de Florin sank into the liquid an incandescent lamp of known lighting power and worked as much as possible at night.



To avoid the personal equation he determined the brightness photometrically. His "transparencemeter" was illustrated in the article. Gillot and Grosjean (*Bull. soc. chim. belg.* **19**, 190) gave an application of the pycnometer method to the determination of the weight and volume of precipitates suspended in liquids.  $p = (D - d')V \times k$ ,  $k = \frac{p}{(D - d')\bar{V}}$ ,  $v = V - \frac{P - p}{d}$ , and

$d = \frac{p}{V - \frac{P - p}{d'}}$ , where  $P$ ,  $D$ ,  $V$  are the total weight, density and

volume respectively of the precipitate and liquid,  $p$ ,  $d$  and  $v$  the corresponding properties of the precipitate alone and  $p'$ ,  $d'$  and  $v'$  those for the clear filtrate, while  $k$  is a constant for each substance. Wagner (*Z. offentl. Chem.* **11**, 404) determined reducing sugars with the Zeiss immersion refractometer. The sugar was reduced as usual with Fehling's solution, the cuprous oxide filtered through an Allihn tube, washed, dissolved in concentrated nitric acid and the solution evaporated to dryness. The residue was taken up with exactly 5 cc. of 2 per cent. nitric acid of refractive index 21.6, diluted to 10 cc. with water and then determined with the refractometer. Ducommun (*Schweiz. Wöchschr. Pharm.* **43**, 635) recommended the use of sodium sulphide instead of ammonium sulphide in analytical separations. Ebler (*Z. anorg. Chem.* **48**, 61) published a general separation of the metals without the use of hydrogen sulphide. It was based upon the varying properties of the metals of forming with ammonia complex cations. Windisch (*Wöchschr. Brauerei*, **22**, 48) continued his examination of asbestos preparations on the market and found that those of Theo. Seitz in Kreuznach were markedly better than those investigated earlier. They contained less water-soluble constituents and the ignition residue of the water extract and the alkalinity were less.

*Combustion and Heating Value.*—Carrasco and Carrasco and Plancher (*Atti accad. lincei* [5], **14**, II, 608, 613) described a new combustion method. The heating is done by electricity inside instead of outside the tube. The absorption apparatus is of the usual form. The special tube and heating apparatus were described. They may be bought of the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin. Considerable work was published upon Dennstedt's simplified combustion method (see his "Anleitung zur vereinfachten Elementaranalyse für wissenschaftliche und technische Zwecke," Meissner's Verlag, Hamburg, 1903). Dennstedt himself (*Z. angew. Chem.* **18**, 1134 and *Ber.* **38**, 3729), also with Hassler and Klünder (*Chem. Ztg.* **29**, 52), gave further details and described various technical applications of the method, such as the determination of oils, coals, sulphur in

pyrite, etc. The apparatus may be bought of Emil Dittmar and Vierth, Hamburg. In the last-mentioned article it was stated that carbon disulphide could be determined by this method and, so far, not by any other. Lippmann (*Loc. cit.* p. 487) took exception to this statement about carbon disulphide, maintaining that this substance could be easily determined by his own combustion method (using cupric oxide-asbestos). Furthermore he claimed that his method is accurate and superior to that by means of platinum-quartz in simplicity and cheapness. Weil (*Ber.* 38, 282), trying Dennstedt's method on the tin chloride double salt of "Violettcarbthiol hydrochloride," found that a crystalline substance sublimed and settled over the platinum quartz, the latter then losing its capacity to glow further. Therefore it would seem that tin like arsenic has a poisonous action upon contact masses. The Heraeus electrical combustion furnace, a modification of which is used by Dennstedt, was described by W. C. Heraeus (*Pharm. Ztg.* 50, 218). In studying the uncommon faults of the combustion method Herman (*Z. anal. Chem.* 44, 686) found that too little attention is paid to the absorption of sulphuric acid and the halogens by the glass tube and contact substances. In trying Dennstedt's method on substances containing nitrogen, sulphur and the halogens he found that for nitrogen and iodine the absorption of gaseous compounds by boats loaded for the purpose could give very good results. In opposition to Calberla (*J. pr. Chem.* 104, 232) he observed that silver at bright redness will not decompose all the oxides of nitrogen, what escapes being absorbed in the soda-lime tube. Lunge and Grossmann (*Z. angew. Chem.* 18, 1249) stated that the Parr calorimeter cannot be used to obtain the heat of combustion of coals giving less than 7500 calories. With coals giving more heat satisfactory results may be obtained, if each degree of corrected temperature be multiplied by 1540 and if their instructions be closely followed. The number 1540 applies only to a Parr calorimeter of such weight as to give with 2000 grams of water the normal water value 2123.

*Gas.*—Lilienfeld (*Ann. Physik.* [4], 16, 931) gave a method for the spectral qualitative analysis of gas mixtures. The tube with outside electrodes and with a capillary fused inside is shunted in parallel to the self-inductor of an electrical circuit consisting of the source of the current, the spark gap and the self-inductor. The band spectrum falls away, the strong lines appear immediately, even with small amounts, the weaker ones after a time dependent upon the conditions of the discharge. The quick disappearance of many lines from the spectrum Lilienfeld explained as a dissociation influence of the second gas which must occur as soon as both gases have a common ion. With low pressure the negative ion of all gases is apparently free electron. He was able to detect 0.7 per cent. helium plainly in nitrogen, at least 0.93 per cent.

argon in nitrogen (probably less), 0.7 per cent. nitrogen in mercury vapor and 0.7 per cent. hydrogen in mercury, the best previous determinations giving about 10, 37, 30. and 30 per cent. respectively. Mason and Wilson (*Pr. Chem. Soc.* 21, 296) found that the white hot mantle could be used as a substitute for platinum asbestos in the preparation of formaldehyde from methyl alcohol and of sulphur trioxide from the dioxide and oxygen, also as a substitute for palladium asbestos in a quartz tube for the combustion of hydrogen or carbon monoxide in air. Pöpel (*J. Gasbel.* 48, 225) devised a scheme for finding the quantity of gas by determining the ammonia. The source of supply was connected with three absorption flasks containing standard sulphuric acid, then with a common gasometer and the gas passed through for a certain length of time. Suppose that before entering the scrubbers the gas contained 8 grams of ammonia per cubic meter and afterwards 1 gram, while the ammoniacal wash-water contained 5 grams per liter for 1000 liters, then  $5000 \div 7$  or 714.3 cubic meters of gas passed through the tube in the time of the experiment. Rimini (*Atti accad. lincei* [5], 14, I, 386) observed that the equation of de Girard and de Saporta (*Bull. soc. chim.* [3], 31, 905) for the decomposition of hydrazine sulphate by copper salts is not true; the copper salt is much more reduced to metallic copper. This copper acting on excess of the hydrazine sulphate gives further amounts of nitrogen even in the cold. Therefore their determination of glucose is not accurate. Their direct determination of sodium nitrite is not usable as was shown by the earlier work of Curtius, Angeli and Dennstedt and Göhlich. Hydrazine sulphate and copper sulphate give, according to Rimini,  $(\text{CuSO}_4(\text{N}_2\text{H}_5)_2\text{SO}_4)_2 + \text{H}_2\text{O}$ .

*Water.*—Cribb and Arnaud (*The Analyst*, 30, 225) published some interesting results upon the action of weakly alkaline waters on iron. Polished pieces of steel or iron plate of a certain size were put into 100 cc. of water; this was maintained at 100° for twenty-four hours, then the iron content of the water was determined. The steel plate was not attacked if the alkalinity (lime, sodium hydroxide or carbonate) of the water exceeded certain limits. With minimal alkalinity the whole surface was attacked, but with rising alkalinity the attack was confined to certain places and was deeper, the total amount of iron dissolved in every case having been about the same. Although the attack on the surface was limited to 1/100 of the original surface the falling off of iron in solution was only 5 per cent. of the maximum amount. Then the solution of iron stopped almost suddenly. The limit with sodium hydroxide and with lime was 10 to 15 cc. of tenth-normal solution, for sodium carbonate 30 to 40 cc. of tenth-normal solution. As a result of special experiments the authors combatted Dunstan's hydrogen peroxide idea of rusting and also

Moody's conception of the action of carbon dioxide in the same process. They could not explain this action of weakly alkaline solutions on iron; it is not electrolytic for no hydrogen is evolved. Eijkman (*Centrl. Bakter. Parasitenk. I*, 37, 742) found that coli bacteria thrive well at 46° while other bacteria do not grow further at this temperature. He took 100 cc. of a spring water, (less of a suspicious sample like a river water), added about one-eighth the water volume of an aqueous solution containing 10 per cent. peptone, 10 per cent glucose and 5 per cent. sodium chloride, then tested in the fermentation flask. The indol test is not as sharp as this one. Gautie (*Ann. chim. anal. appl.* 10, 254) modified the Pere method of quantitatively determining the coli bacilli in drinking-water. Instead of using 100 cc. of water he used varying amounts (80-50-20-10-1 cc.), further 20-15-5-1 drops of the water sample and then correspondingly stepped down the amounts of peptone and 5 per cent. phenol solution added. In most cases it suffices to work with 100-10-1 cc. and one drop. The determination should be set up in duplicate or triplicate to minimize the effect of unequal distribution of the bacilli in the water. Müller (*Z. Hyg.* 51, 1) substituted iron oxychloride for ferric sulphate in Ficker's method of detecting typhus bacilli in drinking-water (precipitation of the water with ferric sulphate and sodium carbonate and solution of the settled or centrifuged precipitate in a 25 per cent. solution of neutral potassium tartrate). Five cc. of "ferri oxychlorati" sufficed for three liters of water.

*Soil.*—Hall (*J. Agr. Sc.* 1, 65), in studying the value of plant ash analysis, reached the conclusion that ascertaining the fertilizer needs of soils by means of plant ash analysis was not to be regarded as a practical method which could replace chemical analysis of the soils. This could only be when some suitable test plant growing everywhere is found which will react with the particular needs of every soil and whose composition at definite times is known. Mehring (*J. Landw.* 53, 229) found that no certain conclusion could be drawn from the determination of the loss of weight on ignition of soils with regard to the three things carbon dioxide or carbonates, chemically combined water and organic matter and that the uncertainty was increased by the use of ammonium carbonate. Neubauer (*Landw. Vers.-Stat.* 63, 141) gave a simple method for the determination of phosphoric acid, potassium, sodium, calcium and magnesium in hydrochloric acid soil extracts. The solution was evaporated to dryness, organic matter destroyed by ignition, the residue washed with water into a 125 cc. flask, boiled for half an hour, diluted up and potassium and sodium determined in 100 cc. of the filtrate (see Neubauer, *Z. anal. Chem.* 39, 481; 43, 14). The insoluble residue and filter are boiled in the same measuring flask with dilute sulphuric acid (an amount equal to 5 cc. of concentrated acid)

for half an hour, diluted and phosphoric acid determined in 100 cc. of the filtrate by the molybdate method, using the molybdate solution prepared without ammonium nitrate. For calcium and magnesium a sample was prepared and heated as before, taken up with water, 2 to 5 grams of ammonium chloride were added, the whole heated on the water-bath till the evolution of ammonia ceased, then washed into a 125 cc. flask, ammonia added, boiled, diluted and the metals determined in 100 cc. of the filtrate as usual. Sjollesma (*J. Landw.* 53, 67) found that the colloid substances of a soil color themselves with suitable coloring materials, whereas quartz grains and unweathered mineral fragments do not to any great extent. Methyl violet (0.1–0.2 gram in 500 cc. water) colors amorphous silica and aluminum silicate. Aqueous solutions of naphthol yellow and Congo red color only amorphous alumina. Alizarin in dilute sodium hydroxide does not color quartz and amorphous silica but does alumina and aluminum silicate. Kaolin is usually not colored. He (*Loc. cit.* p. 70) separated the colloids from quartz grains, etc., by rubbing repeatedly in a mortar with water without breaking up the grains, pouring off the liquid and evaporating it to dryness, then drying in a desiccator, centrifuging for two or three minutes and taking up with a mixture of bromoform and chloroform (sp. gr. 2.5). The solution was filtered after a little standing, washed with ether and dried. Most of the non-colloidal matter he claimed would be removed with one repetition of the centrifuging.

*Mineral.*—Gregory (*Chem. News*, 92, 184) gave a rapid method for the determination of fluorspar. Two grams of substance dried at 120° heated to constant weight gives carbon dioxide with sufficient exactness. Another 2 grams are heated in a platinum dish with pure hydrofluoric acid, the mixture evaporated and ignited, the operation being repeated to constant weight. In the absence of silica the loss of weight on changing calcium carbonate into fluoride is about half the weight of carbon dioxide present. The difference between the weight calculated from the carbon dioxide determination and that after treatment with hydrofluoric acid gives silica, but is not quite accurate in the presence of silicates. A third mass is fumed down with concentrated sulphuric acid. From this weight the amount obtained for silica and the calcium sulphate corresponding to calcium carbonate are subtracted and the remaining increase is a measure of the calcium fluoride converted into sulphate. Lienau (*Chem. Ztg.* 29, 584, 1280) gave a method for the investigation of bauxite. Moisture was obtained by heating for ten hours at 110° in a drying-oven. The loss on ignition was determined by heating 0.5–1 gram of the dried sample to bright redness in platinum; bauxites often contain up to 1 per cent. of organic matter. One gram was taken up with 5–8 cc. of sulphuric acid (1:2) and

evaporated to dryness on an asbestos plate, then taken up with 20 cc. sulphuric acid (1 : 5), boiled, cooled a little, filled up quickly with boiling water and allowed to settle, then filtered. With more than 10 per cent. silica the residue must be fused with primary potassium sulphate. To precipitate titanium dioxide the filtrate was decomposed with 500 cc. of at least 3 per cent. aqueous sulphur dioxide, 50 cc. of 10 per cent. sodium carbonate solution were added, the whole was diluted to 900 cc. with water, heated to boiling for an hour on a sand-bath and filtered. The first 200 cc. might be cloudy and were then poured back through the filter. Hot water containing ammonium chloride was used for washing. The filtrate was evaporated to 500 cc. Fifty or 100 cc. of the solution were reduced with stick zinc wrapped with aluminum wire, poured through glass wool and titrated with tenth-normal permanganate. Alumina and ferric oxide were determined together in 200 or 100 cc., according to the amount of iron.

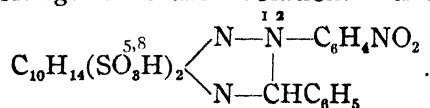
*Volumetric.*—Fuld (*Munch. med. Wochschr.* 52, 1197) stated that common red or blue cabbage boiled in water or allowed to stand twenty-four hours in it made a new indicator, used best with white underneath. It is red in acid and green in alkaline solution.<sup>1</sup> The blue tone in alkaline solution with too much indicator may be removed by a suitable yellow color such as saffron. Petrow (*Pharm. Ztg.* 50, 990) gave also a method of preparing this indicator and said it was capable of general use, but possessed practically no advantages over phenolphthalein or methyl orange. Krebitz (*Seifensiederztg.*, 32, 588) observed that he had used Fuld's indicator for over a year. Hildebrandt (*Wochschr. Brauerei*, 22, 69) gave the following table concerning the usability of certain indicators.

Pellet (*Bull. assoc. chim. suc. dist.* 23, 620) gave reasons for preferring litmus to phenolphthalein for sugar factory work. Rupp and Hartmann (*Arch. Pharm.* 243, 98) gave an oxidimetric method of determining formic acid based upon the following reaction:  $2\text{HBrO}_3 + 5\text{HCOOH} = \text{Br}_2 + 6\text{H}_2\text{O} + 5\text{CO}_2$ . An excess of potassium bromate with dilute sulphuric acid was used and the excess titrated back. Schumacher and Feder (*Z. Unters. Nahr.-Genussm.* 10, 415) found that in this reaction,  $2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$ , if the sulphuric acid were neutralized by say calcium carbonate, only the first precipitated iodine would be titrated and consequently sulphur dioxide could be thus determined. Schwezow (*Z. anal. Chem.* 44, 85) stated that iodine dissolves in benzene with an intense red color, the reaction being more delicate than the starch blue, and he recommended its use in iodometry as an indicator. Margosches (*Loc. cit.* p. 392)

<sup>1</sup> The use of an infusion of red cabbage as an indicator is mentioned in "Comstock's Chemistry," published in Hartford in 1831.—EDITOR.

Indicator.	Titration cold	Titration hot.	Titration to acid.	Titration to alkaline.	Titration and $\text{NH}_4\text{Cl}$ .	Titration and $\text{CH}_3\text{COONa}$ .
1 Phenolphthalein.	Usable only on exclusion of $\text{CO}_2$ .	Usable.	Usable.	Usable.	Not usable.	Usable.
2 Methyl orange.	Usable for N $\text{Na}_2\text{CO}_3$ with $\text{NH}_4\text{Cl}$ , N/10 $\text{Na}_2\text{CO}_3$ with N/10 $\text{HCl}$ and N/10 $\text{HCl}$ with baryta.	Usable.	Usable.	Usable for baryta, only hot.	Usable.	Not usable.
3 Ethyl orange.	Like No. 2.	Usable.	Usable.	Like No. 2.	Usable.	Not usable.
4 Dimethylaminoazobenzene.	Like No. 2.	Usable only in solution.	Usable.	Like No. 2.	Usable.	Not usable.
5 Sodium alizarin-sulphonate.	Usable even with small amounts of $\text{CO}_2$ .	Usable except with N $\text{Na}_2\text{CO}_3$ to alkaline.	Usable.	Usable for baryta, not for N $\text{Na}_2\text{CO}_3$ .	Usable.	Not usable.
6 Alizarin.	Like No. 5.	Like No. 5.	Usable.	Like No. 5.	Usable.	Not usable.
7 Carmine acid.	Usable.	Usable only with N $\text{Na}_2\text{CO}_3$ to alkali.	Usable only cold.	Usable for baryta and hot N $\text{Na}_2\text{CO}_3$ .	Usable.	Not usable.
8 Congo red.	Usable except with N $\text{Na}_2\text{CO}_3$ to alkaline.	Not usable.	Usable.	Usable only for baryta.	Usable.	Not usable.
9 <i>p</i> -Nitrophenol	Like No. 8.	Like No. 5.	Usable.	Like No. 8.	Usable.	Not usable.
10 Azolitmin.	Like No. 5.	Usable.	Usable.	Usable.	Usable.	Not usable.
11 Lacmoid.	Usable except N/10 $\text{Na}_2\text{CO}_3$ with N/10 $\text{HCl}$ .	Usable.	Usable.	Usable.	Usable.	Not usable.
12 Rosolic acid.	Usable for N $\text{Na}_2\text{CO}_3$ and N $\text{HCl}$ and N/10 $\text{HCl}$ with N/10 baryta.	Usable.	Usable.	Usable.	Use not advisable.	Not usable.
13 Litmus. •	Like No. 1.	Usable.	Usable only on exclusion of $\text{CO}_2$ .	Usable only on exclusion of $\text{CO}_2$ .	Usable.	Not usable.

stated that this use of benzene had been given by Moride in 1852, and that he himself with Ditz had recommended toluene in 1904. Woods (*J. Chem. Ind.* **24**, 1284) gave a new indicator prepared by boiling 23 grams of the condensation product from diazo-*p*-nitraniline and 2, 5, 7-aminonaphtholdisulphonic acid with 5.5 grams of benzaldehyde, 100 grams of hydrochloric acid (18° Bé.) and 900 grams of water for fifteen minutes. It is colorless in acid, intense orange in alkaline solution. Its formula is



Sörensen and Andersen (*Z. anal. Chem.* **44**, 156), Sebelien (*Chem. Ztg.* **29**, 638) and Lunge (*Z. angew. Chem.* **18**, 1520) discussed further the relative merits of sodium oxalate and sodium carbonate as the standard for titrations. The first-named gave their reasons for preferring the oxalate; an acid standardization by means of this substance offers absolutely no difficulty and the decomposition products of the oxalate are always the same no matter how it is decomposed so long as an alcohol flame is used as the source of heat. They observed that titration with sodium carbonate dried according to Lunge gives about the same results as those with the oxalate. The difference is never 0.1 per cent. and usually comes from the fact that the carbonate has given off a little more carbon dioxide than it has retained water. Sodium carbonate free from water, hydroxide and bicarbonate can, apparently, not be prepared. These authors further prefer phenolphthalein to methyl orange for scientific work. Sebelien decided also in favor of sodium oxalate, saying that in the calcination of sodium carbonate some hydroxide is always formed. Its hygroscopicity is also very great, while the oxalate is fully unhygroscopic. Lunge showed that heating the oxalate with illuminating gas is as good as with alcohol, if the crucible is put into an asbestos plate with a hole of proper size to carry the crucible. He stated that the indicator used in standardization must be the one used in the titrations. Sodium carbonate dried at 270° he found to contain no hydroxide or entirely negligible traces. The carbonate is not so hygroscopic in a well-closed weighing-bottle in a desiccator; 17.9856 grams weighed after fourteen days 17.9862 grams. He stated that in moist air the oxalate also takes up water. Lunge stated further that primary sodium carbonate, recommended by North and Blakey (*J. Chem. Ind.* **24**, 395) as a reliable indicator, will lose some carbon dioxide even in closed vessels.

*Microscopic.*—Di Cristina (*Z. wiss. Mikrosk.* **22**, 99) gave a new method of joining together sections of material embedded in celloidin. The sections are put for a very short time in 94 per cent. alcohol, then placed upon an object glass covered with a



layer of five parts egg albumen and one part neutral glycerol. They will then stand even treatment with absolute alcohol to remove the celloidin. Grigorjew (*Vrtljschr. ger. Med. u. öffentl. Sanitätswesen*, 29, 79) recommended 10 per cent. formalin solution for the preservation of organs and their contents for subsequent investigation. He stated it to be better than alcohol. Lamb (*Collegium*, 1905, 151) and Priestman (*J. Chem. Ind.* 24, 231) described the preparation of specimens and the microscopic structure of genuine sumach and its chief adulterants. Ostwald (*Sitzungsber. Kgl. pr. Akad. Wiss.* Berlin, 1905, 167) gave some microscopic reactions for the detection of drying oils and the nitrogen-bearing cementing materials like glue, albumen and casein. Raehlmann (*Vortrag vor dem Kongress zur Bekämpfung der Farben- und Malmaterialien Verfälschung zu München*. Protokoll 23, Weimar) observed by microscopic study of cross-sections of paintings that oil was very little used by such painters as Titian, Tintoretto and the old Dutch and German masters and that where it was used it had already gone over into varnish. Painters of the German and Dutch hey-day of the art put their colors on in distinctly separated layers. They knew how to prevent chemical decomposition and change in neighboring layers for they put in between separating indifferent layers. Pavlow (*Z. wiss. Mikrosk.* 22, 186) used creosote as a water-extracting material for embedding in paraffin. The objects, fixed in any solution, were put into creosotum fagi (without preliminary dehydration) for four to twenty-four hours according to their size, then two to three hours in pure creosote, the excess of this removed by filter-paper, the objects then put for an hour in xylene or toluene and finally embedded in paraffin.

#### ANALYSIS OF INORGANIC COMPOUNDS.

*Metallouls, Oxygen.*—Dickson (*The Analyst*, 30, 145) stated that for the determination of oxygen in copper by heating in a stream of hydrogen the copper must be subdivided as much as possible or larger pieces can be used if a metal of lower melting-point like tin be added to the copper. Archbutt (*Loc. cit.* p. 385) said that the simpler method is reliable even if the turnings are larger; the larger the pieces the slower the determination simply. Jorissen and Ringer (*Chem. Weekblad*, 2, 781) compared the methods of Romijn and Bjerrum for the determination of oxygen dissolved in sea-water. Experiments with artificial solutions containing salt, calcium and magnesium chlorides showed that in the presence of 11.32 per cent. magnesium the method of Romijn gave about 88 per cent. too low a value for the oxygen content of the water, while the method of Bjerrum in the presence of 0.43 per cent. calcium gave 10 to 13 per cent. too low results. The presence of sodium has no effect. Legler (*Pharm. Centrhl.* 46, 272) determined the oxygen in water by means of sodium

sulphite. He filled a glass-stoppered flask of 300–600 cc. with the water and added 5 cc. of sulphite solution (5 grams  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  in 250 cc. water) through a pipette to the bottom of the flask. He mixed the liquids, poured the contents of the flask into a measured excess of iodine solution and titrated back with thiosulphate. The pipette is used in the same way in standardizing the solutions. In one liter of water, if 5 cc. of sulphite

solution and 10 cc. of iodine solution are used,  $O = \frac{1000}{V-m} f(n-m) \frac{O}{100}$ ,

where  $V$  is the flask volume,  $m$  the number of cubic centimeters of thiosulphate used in standardization,  $n$  the number used in the determination,  $O$  the number of milligrams of oxygen corresponding to 100 cc. of iodine solution and  $f$  a factor giving the relation of the thiosulphate and iodine solutions. Noll (*Z. angew. Chem.* **18**, 1767) gave a modification of Winkler's determination of oxygen in water. Noll's manganese solution consisted of 2 cc. of a 50 per cent. manganese chloride solution, 2 cc. of a 40 per cent. sodium hydroxide solution and 20 cc. of water shaken together in a capacious flask till brown, then 50 cc. of concentrated hydrochloric acid were added and the solution made up to 300 cc. with distilled water. Then he added to 100 cc. of distilled water and to 100 cc. of the water sample each 10 cc. of 5 per cent. potassium iodide solution, and then 25 cc. of the manganese solution, allowed the mixture to stand five minutes and determined the iodine liberated. Rumpel (*Apoth. Ztg.* **20**, 984) found that many medicinal hydrogen peroxide solutions contain too much acid. Chemically pure 3 per cent. peroxide requires for 100 cc. 1–1.2 cc. of tenth-normal potassium hydroxide. For medicinal purposes the peroxide should require not more than 1 cc. of normal caustic potash for 100 cc. Rumpel found that four of thirty-four samples exceeded this. Schmatolla (*Pharm. Ztg.* **50**, 641) would allow in hydrogen peroxide a maximum of 0.01 per cent. chlorine. He gave this test for the peroxide; 200 cc. of the water containing it are acidified with five to ten drops of dilute sulphuric acid, five to eight drops of a 1 per cent. solution of cobalt nitrate are added and then caustic potash solution in drops. The solution will be colored brown through the formation of cobaltic hydroxide in presence of 0.5–1 mg. of peroxide in one liter.

**Sulphur.**—Bender (*Z. angew. Chem.* **18**, 293) gave the modification of the Eschka sulphur determination used in the Westphalian Laboratory; the mixture of coal and soda-magnesia is heated in a short hard glass tube 18 cm. long, 3 cm. in diameter, with one end closed, the tube being held horizontal in a burette holder. At the end of the burning a porcelain dish is put under the tube because the latter usually breaks on cooling. Blacher and Koerber (*Chem. Ztg.* **29**, 722) determined combined sulphuric

acid volumetrically by titrating the boiling solution, after addition of 1 cc. of tenth-normal soda solution and alcohol and phenolphthalein for indicator, with tenth-normal barium chloride to disappearance of the color. Brunck (*Z. angew. Chem.* **18**, 1560) gave a new method of determining sulphur in coal. One gram of the finely powdered coal was mixed with 2 grams of a mixture of dehydrated sodium carbonate (one part) and cobaltic oxide (two parts), the mixture put into a roomy porcelain or platinum boat and this into a 30 cm. combustion tube. Oxygen was passed through and the end of the boat away from the oxygen entrance heated with a small flame to glowing. The rest of the burning was regulated by the oxygen addition, the combustion being complete when the glowing ceased. On cooling, the contents of the boat were extracted with a little warm water, filtered and washed with water containing soda to prevent clouding. The alkaline filtrate was warmed with some hydrogen peroxide to oxidize possible sulphide, the solution acidified and the sulphuric acid precipitated as barium sulphate. The cobaltic oxide might hold some of the acid back, presumably as basic sulphate; in this case the residue was dried, dissolved in hydrochloric acid after ignition of the filter and precipitated with barium chloride. Jene (*Chem. Ztg.* **29**, 362) stated that the wet method of solution in nitric acid and precipitation of the sulphuric acid for determining sulphur in burned pyrites is inaccurate, the results being sometimes 1.5 per cent. lower than those obtained by the Fresenius fusion method. Gottlieb (*Loc. cit.* p. 688) observed that this was due to the fact that some pyrites contain in their ignition residues as much as 8.5 per cent. of barium oxide which would combine with 1.8 per cent. of sulphur. Mennicke (*Loc. cit.* p. 495) did not agree with Jene that the wet method of oxidation is entirely unusable. He stated that it depended upon the purpose of the sulphur determination and that the wet method gives the residual usable sulphur in the residues. Krug (*Stahl und Eisen*, **25**, 887) gave a method of avoiding the evils of the ordinary methods for the determination of sulphur in iron. He treated the iron chloride solution with moist silver oxide, all the iron being removed as hydroxide and the chlorine as silver chloride, and the sulphuric acid being left in the filtrate. The method he stated is tedious but will serve as a standard. He recommended for a rapid determination the separation of the iron chloride by Rothe's ether method. Silberberger in 1903 criticized Lunge's twenty-year-old method of determining sulphur in pyrites and proposed, instead of precipitating with barium chloride, to precipitate the sulphuric acid from solution acidified with hydrochloric acid by means of 10 per cent. alcoholic strontium chloride and subsequent addition of 95 per cent. alcohol. He washed the strontium sulphate with alcohol and ignited it at a low temperature. Dennstedt and

Hassler (*Z. angew. Chem.* **18**, 1562, 1903) pointed out that the error of some basic sulphate forming in Lunge's method and not dissolved by his, "1 cc. of hydrochloric acid in 100 cc. of hot water," might be avoided by adding the 1 cc. of concentrated acid to the dry residue after driving off the nitric acid, heating and then adding the 100 cc. of hot water. They stated there was nothing else wrong with the Lunge method. Then they gave the details of their simplified combustion method for determining sulphur in pyrites. Lunge, and Lunge and Stierlin (*Loc. cit.* pp. 449, 1656 and 1921) stated that a number of chemists had tried comparatively his method and Silberberger's and found the latter inaccurate, though sometimes good results were obtained through compensation of errors. He stated that he always added his "1 cc. of hydrochloric acid in 100 cc. of hot water" as Dennstedt and Hassler recommended and that that was what he meant. He gave as an explanation of the varying results of different chemists using his method not the formation of basic sulphate but the greater or less occlusion caused by the manner of adding the barium chloride. If the hot dilute barium chloride were added all at one pouring, more of it was occluded in the precipitate than if it were poured slowly. This was pointed out by Hintz and Weber and if their directions were followed for the precipitation, using Lunge's for the rest, the different errors in the determination were almost entirely compensated. Lunge stated also that Dennstedt and Hassler's combustion method of determining usable sulphur in pyrites is rational, but takes more time and apparatus than his own. The first of his articles is the report of the ninth sub-committee of the International Committee on Analysis of the Sixth International Congress for Applied Chemistry at Rome. H. S. Pattinson (*J. Chem. Ind.* **24**, 7) found that Silberberger's method will give accurate results but is more tedious and expensive than Lunge's, and gave a slight modification of the latter. J. Pattinson and Dunn (*Loc. cit.* p. 10) pointed out as sources of error in the sulphur determination that sulphur can come from the rubber stoppers used in the wash-bottles and also that pure barium chloride of commerce often contains sulphur. Von Knorre (*Die Chem. Ind.* **28**, 2) stated that Lunge's method is better than Silberberger's. He found also that the use of benzidine hydrochloride proposed by Muller and Dürkes (*Z. anal. Chem.* **42**, 477) and especially the modification of their method given by Raschig (*Z. angew. Chem.* **16**, 818) is a widely usable and pretty method for the rapid volumetric determination of sulphuric acid, good enough for all technical and for most scientific purposes. This was confirmed by Huber (*Chem. Ztg.* **29**, 1227). Matwin (*Z. angew. Chem.* **18**, 1766) recommended that the sulphur in liquid combustibles be determined by burning the substance in the Drehschmidt apparatus for sulphur determination in gaseous

combustibles. He would weigh the substance in a little spirit or oil lamp with a wick and then burn it from this. Pfeiffer (*J. Gasbel.* 48, 977) determined sulphur in gas purification substances by burning 1 gram of the sample in a flask filled with oxygen and containing 25-50 cc. of sodium hydroxide. If the substance did not contain enough sulphur to burn, he poured glycerol over it and stuck a lighter in it. After absorption of the gases of combustion he added to the flask 1 cc. of 30 per cent. hydrogen peroxide and after mixing titrated the excess of alkali with normal acid and methyl orange. One cc. of alkali is equivalent to 1.6 per cent. sulphur.

*Selenium and Tellurium.*—Berg (*Bull. soc. chim.* [3], 33, 1310) gave a method for the determination of tellurium which rests upon the formation of tellurium chloride and the ease with which this compound can be volatilized. The determination was carried out in a combustion tube drawn out and bent at right angles. The other end was connected with a hydrochloric acid generator. The substance was placed in a boat near the bend, the air displaced by hydrochloric acid gas and the tube then heated gently. The tellurium chloride volatilized and was collected in a little U-tube containing water. Gosio (*Atti accad. lincei* [5], 14, II, 188) recommended the use of selenites and especially tellurites for the detection of bacteria. Tellurites give a black and selenites a red precipitate with them.

*Halogens.*—Dittrich and Bollenbach (*Ber.* 38, 751) gave a new method for the analysis of perchlorates. They put in a large platinum or nickel crucible first a layer of sodium nitrite (chlorine-free), then the weighed substance carefully in the middle, then more nitrite, in all about 6 grams of the latter. When all melted, the mass was kept at as low a temperature as possible for half an hour, then it was extracted with warm water, silver nitrate and nitric acid added, the nitrous acid driven off on a water-bath and the silver chloride determined. Stepanow (*J. russ. physik.-chem. Ges.* 37, 12) split off halogen bound to ring carbon atoms by means of sodium and alcohol. A little tube with the weighed substance was brought into an Erlenmeyer flask containing 20-40 cc. of 98 per cent. alcohol, the flask connected with a vertical condenser and heated on a water-bath. Small pieces of sodium were thrown into a flask through the condenser tube, about twenty-five times the theoretical amount of sodium being required. At the end of the reaction 20-40 cc. of water were added, then nitric acid to strongly acid reaction and the halogen was titrated according to Volhard. The reaction was first used by A. Baeyer (*Ber.* 12, 459) for this purpose. Wentzki (*Z. angew. Chem.* 18, 696) gave a new method of separating the halogens in halide mixtures. He used mercurous halides to precipitate the halides in solution as for example mercurous chloride or bromide to precipitate mercurous

iodide from a solution of potassium iodide. In a mixture of all three he determined in an aliquot portion of the solution the combined silver salts, then in a portion he precipitated iodine with mercurous bromide and determined in the filtrate silver chloride and bromide. In another he removed iodine and bromine with mercurous chloride and determined the silver chloride in the filtrate. Ehrenfeld (*Chem. Ztg.* **29**, 440) separated hydrofluoric and sulphuric acids by precipitating both as barium salts, and treating with calcium chromate in acid solution when barium fluoride is transposed and barium sulphate is not. Merck (*Pharm. Ztg.* **50**, 1022) gave a dry test for iodine compounds. He rubbed the compound with potassium persulphate and some soluble starch when a blue color was obtained in the presence of oxygen-free iodine compounds.  $K_2S_2O_8 + 2KI = I_2 + 2K_2SO_4$ . Iodates he reduced to iodides by rubbing with zinc powder.  $I_2O_5 + 6Zn = ZnI_2 + 5ZnO$ .

*Nitrogen*.—Barbieri (*Chem. Ztg.* **29**, 668) gave a volumetric method for the determination of nitrous acid based upon this reaction,  $2Ce(SO_4)_2 + KNO_2 + H_2O = Ce_2(SO_4)_3 + KNO_3 + H_2SO_4$ . The end-point is the disappearance of the yellow color of the ceric solution. It is better, though, to add an excess of the ceric solution and titrate back with potassium iodide. The oxidizing power of the ceric solution is determined iodometrically or according to Knorre. Bensemann (*Z. angew. Chem.* **18**, 816, 939, 1225) gave a method for the analysis of salt-peter. He dissolved 8 grams of the sample in water, diluting to 1000 cc. He determined chlorine and sulphuric acid in 50 cc. portions. He evaporated 100 cc. repeatedly to dryness with 16 grams of oxalic acid, finally igniting for fifteen minutes and dissolving in water to 250 cc. He determined the chlorine in 125 cc.  $AgCl \times 24.146 = \text{per cent. } KClO_4$ . He titrated 100 cc. with twice normal acid. The acid used represents nitrate and original chloride, also chloride from chlorate and perchlorate. To determine chlorate 20 grams of salt-peter were mixed according to Gilbert with pyrolusite and some sodium carbonate solution, the mixture dried, melted and ignited. The residue was dissolved in water and the chlorine determined gravimetrically.  $(AgCl - (AgCl \text{ for } NaCl \text{ and } KClO_4)) \times 21.359 = \text{per cent. } KClO_3$ . Brown (*Pr. Chem. Soc.* **21**, 208; *J. Chem. Soc.* **87**, 1051) determined organic nitrogen in drinking-water by treating 200 cc. of the sample with potassium hydroxide and permanganate, evaporating to dryness and igniting. The determination was carried out in a retort of Jena glass or copper and the ammonia determined with Nessler's reagent. Busch (*Ber.* **38**, 861) used his newly discovered diphenylenedianilodihydrotriazole ("nitron,"  $C_{20}H_{16}N_4$ ) for the gravimetric determination of nitric acid. The reagent may be used also to test qualitatively for the acid, best as a 10 per cent. solution in 5 per cent.

acetic acid. To 5 or 6 cc. of the solution to be tested is added one drop of dilute sulphuric acid, then 5 or 6 cc. of the nitron solution. The formation of a precipitate can be detected with one part of acid in 60,000 parts of water at room temperature or in 80,000 of water at zero. A number of other salts of nitron are difficultly soluble; bromide 1:800, iodide 1:20,000, nitrite 1:4,000, chromate 1:6,000, chlorate 1:4,000, perchlorate 1:50,000, sulphocyanate 1:15,000, also the ferro- and ferricyanides and the picrate. Quantitatively an amount of substance equal to 0.1 gram of nitric acid is dissolved in 80–100 cc. of water, ten drops of dilute sulphuric acid added, the mixture heated nearly to boiling and then the nitron acetate solution added. The whole is allowed to stand for one and a half to two hours in ice water, the precipitate separated by suction in a Neubauer crucible and washed with as little ice water as possible. The weight is constant after drying at  $110^{\circ}$  for three-quarters of an hour and multiplied by one-sixth (better  $63/375$ ) gives nitric acid. Nitrites must be previously destroyed with hydrazine salts. Gutbier (*Z. angew. Chem.* **18**, 494) fully confirmed Busch's claims for nitron for the above purpose. Busch (*Z. Unters. Nahr.-Genussm.* **9**, 464) said the nitron could be used for the determination of nitric acid in water. Flaman and Prager (*Ber.* **38**, 559) state that compounds which contain phenylhydrazine or which split it off are not satisfactorily determined by the Kjeldahl method because of the resistance of phenylhydrazine to reduction. They recommended this procedure. The substance (0.15 to 0.2 gram) is dissolved in 10 cc. of alcohol in a 500 cc. Kjeldahl flask and heated with 0.5–1 gram of zinc dust and 2 to 5 cc. of hydrochloric acid (sp. gr. 1.19) to decolorization; this happens usually in a few minutes. Ten cc. of concentrated sulphuric acid and 0.5 gram of crystallized copper sulphate are added and the mixture heated to the beginning of the evolution of white fumes. Then 6 grams of powdered potassium sulphate are added and the heating continued till the liquid is clear and bright green, usually a quarter of an hour. The rest of the determination is as usual. Alvarez (*Chem. News* **91**, 155; *Bull. soc. chim.* [3], **33**, 717; *Gaz. chim. ital.* **35**, II, 427), Bay (*Compt. rend.* **140**, 796), Frerichs (*Arch. Pharm.* **243**, 80) and Hinrichs (*Bull. soc. chim.* [3], **33**, 1002) all pointed out that the diphenylamine blue color is not a characteristic test for nitric acid, but is given by other oxidizing agents. Alvarez used a sulphuric acid solution of mixtures of diphenylamine with resorcinol and with  $\beta$ -naphthol and described the colors accurately in distinguishing between nitrates, nitrites and chlorates. Frerichs shook the nitric acid out with ether, added some grains of diphenylamine, then carefully the sulphuric acid. A yellow color due to bromine, iodine or chromic acid he removed by shaking with some aqueous sulphur dioxide, then trying the

diphenylamine reaction on the filtered ether. Hinrichs replaced the concentrated sulphuric by concentrated hydrochloric acid and stated that this gave with nitric acid and diphenylamine in the cold no reaction, but on warming to  $50^{\circ}$  or with dilute solutions even to boiling the blue color was obtained. Nitrites and many other oxidizing agents give the blue color in the cold. Meisenheimer and Heim (*Ber.* **38**, 3834) arranged an apparatus so that the following reaction might be carried out in a carbon dioxide atmosphere and the nitric oxide measured.  $\text{HNO}_2 + \text{HI} = \text{NO} + \text{I} + \text{H}_2\text{O}$ . Then, if present, they determined nitric acid after the nitrous acid by the use of ferrous chloride and hydrochloric acid.  $\text{HNO}_3 + 3\text{FeCl}_2 + 3\text{HCl} = \text{NO} + 3\text{FeCl}_3 + 2\text{H}_2\text{O}$ . This nitric oxide they measured in a second eudiometer. The method was criticized by Raschig (*Loc. cit.* p. 3911) who said there was little need for such methods and who pointed out that the determination might be more quickly made by titrating the iodine with thiosulphate. Meisenheimer and Heim (*Loc. cit.* p. 4136) replied that the method was intended for the determination of both acids when present together and that under those conditions the iodine could not be titrated with thiosulphate. Sorensen and Andersen (*Compt. rend. des trav. d. Lab. d. Carlsberg* **6**, 193; *Z. physiol. Chem.* **44**, 429) advanced as the reason why the ordinary Kjeldahl method will not do for lysine and its derivatives the formation of ring-formed piperidine compounds caused by the concentrated sulphuric acid. Piperidine and its compounds do not give up all their nitrogen as ammonia in the ordinary Kjeldahl but do in the Gunning modification or that of Arnold and Wedemeyer. Trillat and Tournet (*Compt. rend.* **140**, 374; *Bull. soc. chim.* [3], **33**, 304, 308) gave a new test for ammonia in water.  $3\text{Cl} + \text{NH}_3 + 3\text{NaOH} = 3\text{NaCl} + \text{NI}_3 + 3\text{H}_2\text{O}$ . They treated 20 to 30 cc. of the water to be tested with three drops of a 10 per cent. potassium iodide solution and two drops of a saturated alkaline hypochlorite solution and compared the black color with that of standard solutions. The reaction they claimed is visible at one part in 500,000 and that the error does not exceed 1:10,000. Amines, amides, ureides, pyridine derivatives, nitrates and nitrites do not affect the reaction but saliva, the gastric juice, urine and meat juices give it. There is a small amount of iodine set free in the test, causing a slight yellow color which the authors said does not interfere with the color determination. In doubtful cases a comparative test with pure water can be made. A very slight excess of hypochlorite will destroy the color of the iodine while only weakening very slightly the color of the nitrogen iodide. The iodine may also be removed by chloroform. Cavalier and Artus (*Bull. soc. chim.* [3], **33**, 745) have tried to use this reaction for the determination of ammonia in drinking-water, but found that its lack of delicacy (2 mg. of ammonia in one liter) excluded its direct use with most



drinking-waters. A strong concentration by evaporation is necessary and this removes its chief supposed advantage over the Nessler method. The nitrogen iodide disappears rapidly; the color faded for them in one minute and was entirely gone in two or three, so the colorimetric determination is very uncertain. Winteler (*Chem. Ztg.* **29**, 689, 1009) criticized Lunge and Rey's tables for the relation of content and density of highly concentrated nitric acid solutions and gave new tables of his own, differing as much as 2.5 per cent. in some places from theirs. Lunge, Veley and Manley, and Putzer (*Loc. cit.* pp. 933, 1072, 1207 and 1221) all contested the accuracy of Winteler's work.

*Phosphorus*.—Arnold and Werner (*Loc. cit.* p. 1326) studied the behavior of the three phosphoric acids toward twenty-three reagents and found that the customary reactions for their detection are almost all useless. They proposed the following tests: For orthophosphate: cobalt meta- and pyrophosphates are reddish in color, soluble in excess of the phosphate but insoluble in acetic acid, while cobalt orthophosphate is blue, insoluble in excess of the phosphate and soluble in acetic acid. For metaphosphate: with cobaltamine solution the metaphosphate gives a brown precipitate soluble in excess of the metaphosphate, while ortho- and pyrophosphates do not give precipitates. Alkaline bismuth solution also precipitates only the metaphosphate, white, soluble in excess of the phosphate. For pyrophosphate: they used copper or cadmium salts in acetic acid solution. The copper pyrophosphate is a blue-white precipitate soluble in excess of the pyrophosphate, while the ortho- and meta-salts are not precipitated. The cadmium salt is a white precipitate insoluble in excess of the pyrophosphate. Cadmium metaphosphate is also precipitated under proper conditions but it is soluble in excess of metaphosphate. Dinan (*Mon. scient.* [4], **19**, 94) determined phosphorus in phosphor-bronze thus: He dissolved 3.5 grams of the bronze in 1:1 nitric acid, filtered, washed the residue, boiled the filtrate in a beaker with 7 grams of oxalic acid and 7 grams of ammonium oxalate till a clear solution was obtained. The solution he electrolyzed at 65–70°, with a current of 3.5–4 volts and 0.5–0.7 ampere per square decimeter, adding oxalic acid from time to time. In the filtrate he precipitated the phosphoric acid as phosphomolybdate, dried at 100° and weighed. The phosphoric acid may be precipitated after the addition of 5 grams of citric acid as the ammonium magnesium compound. Hissink and Van der Waerden (*Chem. Weekblad*, **2**, 179) discussed the formula of the phosphomolybdate precipitate and the effect of adding sulphuric acid to the solution before precipitation. They gave the following procedure for the determination of water-soluble phosphoric acid in superphosphates, etc. Twenty grams of the substance were shaken for thirty minutes with 900 cc. of

water and this diluted to 1000 cc. To 5 cc. of the solution were added 10 cc. of nitric acid, 15 of ammonium nitrate, 25 with 25 mg. of sulphuric acid, the mixture was heated according to Pemberton (without the Petermann liquid) and then precipitated with 10+5 cc. of molybdate solution. The precipitate has the composition  $(\text{NH}_4)_3\text{PO}_4 \cdot 12.65 \text{ MoO}_3$  and is dissolved by 24.3 molecules of sodium hydroxide. Raschig (*Z. angew. Chem.* **18**, 374, 953) determined phosphoric acid thus: He dissolved a weight of sample giving close to, but not more than, 0.15 gram of  $\text{P}_2\text{O}_5$ . This was precipitated in an Erlenmeyer flask with magnesia mixture and the precipitate gathered upon a double horizontal suction filter 40 mm. in diameter, using the clear filtrate to get all the precipitate upon the filter. The mother-liquor was sucked off as completely as possible and the precipitate washed twice, once with 10 cc. of water, then 5 cc., sucking the precipitate as dry as possible each time. After raising the diminished pressure the filter and contents were transferred to a beaker, using not more than 20 cc. of water for washing, a drop of methyl orange added and the solution titrated, stirring or shaking, with hydrochloric acid. The color change is sharper according to Schucht if a blue glass is used for then when the liquid reaches acid reaction it appears through the glass suddenly green. Raschig claimed that his method is simpler than that of Hundeshagen to which Hlavnicka (*Loc. cit.* p. 655) called attention. Schenke (*Landw. Vers.-Stat.* **62**, 3) pointed out that the Association method (citrate) of determining phosphoric acid gives too low results compared with the Märcker method (molybdate), in the mean about 0.38 per cent. too low; but if the acid solution were nearly neutralized with ammonia and only 50 cc. instead of 100 cc. of ammonium citrate solution used, very nearly the same result was obtained as with the molybdate method. Böttcher (*Chem. Ztg.* **29**, 1293) said that his own work as well as the earlier work of Märcker, Halencke and Mach showed that Schenke is wrong. Vignon (*Compt. rend.* **140**, 1449; *Bull. soc. chim.* [3], **33**, 805) detected free white phosphorus in phosphorus sulphide by passing a stream of hydrogen over the sulphide. The presence of the phosphorus is shown by the phosphorescence of the hydrogen and the green flame of the gas when burned (with formation of phosphoric acid).

*Arsenic and Antimony.*—Cantoni and Chaptens (*Arch. sci. phys. nat. Genève* [4], **19**, 364) separated arsenic and antimony by placing the solution with concentrated hydrochloric acid and methyl alcohol in a 250 cc. distilling flask connected with a condenser whose small end dips into a solution of sodium hydroxide. Through the cork of the distilling flask there was a movable glass tube shoved and kept within a few millimeters of the liquid

level. Dry air passed through the flask at room temperature will remove the arsenic completely from the flask. Antimony does not volatilize under these conditions. Mai and Hurt (*Z. Unters. Nahr.-Genussm.* **9**, 193) described an electrolytic determination of small amounts of arsenic. They used a U-tube with platinum foil electrodes; one end of the tube had a simple liquid trap, the other a 25 cc. dropping funnel whose end dipped under the solution and a delivery tube connected through a calcium chloride tube containing pumice saturated with alkaline lead solution to stop hydrogen sulphide with a bulbed absorption apparatus. The electrolyte was 12 per cent. sulphuric acid and the absorption tube contained 10 cc. of hundredth-normal silver nitrate solution. The purity of the reagents having been tested by running the current and letting the hydrogen bubble through the silver nitrate for an hour, the suspected arsenic solution (not over 10 cc.) was run in slowly from the dropping funnel without interrupting the current, then washed in with a little water. With arsenic the silver nitrate blackens and in two to three hours the reduction is complete. The contents of the absorption tube were washed through an asbestos filter, rinsed with 3 or 4 cc. of water, then titrated with hundredth-normal sulphocyanate. One cc.  $\text{AgNO}_3 = 0.1655$  mg.  $\text{As}_2\text{O}_3 = 0.1916$  mg.  $\text{As}_2\text{O}_5$ . The lower limit of the determination is about 1/50 mg. For qualitative purposes the silver nitrate in the first bulb of the absorption tube will blacken with amounts down to 0.0005 mg. The bulbs can also be replaced by the ordinary dry tube for the Marsh test mirror. The authors used a current of six to eight volts and two to three amperes. The apparatus may be bought of Wagner and Munz in Munich. Similar experiments have been tried by Bloxam and by Trotman. Frerichs and Rodenberg (*Arch. Pharm.* **243**, 348) gave a slight modification of part of the Mai and Hurt apparatus; they prefer the cell of Trotman (*J. Chem. Ind.* **23**, 177). Mai (*Z. Unters. Nahr.-Genussm.* **10**, 290), instead of totally destroying organic matter before testing for arsenic, obtained a coal-like mass by treating the dried substance with its weight of fuming nitric acid containing 5 per cent. of sulphuric acid and gradually driving this off. The residue he distilled with five or six times its weight of hydrochloric acid (sp. gr. 1.19) and distilled off one-fourth to one-third the liquid; all the arsenic goes over as the trichloride. The distillate he treated with one-fourth its volume of nitric acid, evaporated almost to dryness, then added cautiously sulphuric acid and heated to the appearance of white fumes. This he diluted and electrolyzed in the Mai and Hurt apparatus. Vitali (*Boll. chim. farm.* **44**, 49) observed that the yellow compound formed by the action of arsine on mercuric chloride ( $\text{AsHg}_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ ) can be used as a test for mercury, 0.001 to 0.0001 gram of mercuric

chloride with zinc, hydrochloric acid and arsenious oxide giving the color. It was noted in 1890 by Franceschi that in testing for arsenic one had to look out for mercury compounds, especially mercuric chloride. Vitali found that stibine and phosphine give similarly colored compounds. Vortmann and Metzl (*Z. anal. Chem.* **44**, 525) precipitated antimony quantitatively as the trisulphide by heating to boiling the solution containing for each 100 cc. 24 cc. of concentrated hydrochloric acid, placing the containing vessel in a boiling water-bath and passing in a rapid current of hydrogen sulphide. The precipitate was at first yellowish, then redder and finally quickly black; the precipitation was accomplished in thirty to thirty-five minutes. The solution was then diluted with the same volume of water and the treatment with hydrogen sulphide repeated. The precipitate was filtered through a Gooch crucible, washed with water, then alcohol and heated in a current of carbon dioxide to  $270-280^{\circ}$ . Or it is simply dried for twenty to thirty minutes at  $110^{\circ}$ , allowed to cool and weighed. The precipitate might be filtered on to a paper filter and ignited in a weighed crucible containing a weighed amount of a mixture of three parts of ferric oxide and one part of ferric nitrate. On ignition the trisulphide would be converted into the pentoxide. Knowing the amount of ferric oxide coming from ignition of the weighed amount of the iron mixture by previous experiment the excess in weight gives the weight of the antimony pentoxide. Antimony they separated from tin by dissolving the sulphides of both metals in 1:1 hydrochloric acid, neutralizing with sodium carbonate or hydroxide, using phenolphthalein, diluting to a definite mark (50-60 cc.), adding the same volume of concentrated phosphoric acid (sp. gr. 1.3) and for every 100 cc. 20 cc. of concentrated hydrochloric acid, then treating with hydrogen sulphide as above. Antimony trisulphide was precipitated.

*Carbon, Boron and Silicon.*—Goutal (*J. Gasbel.* **48**, 1006) gave an equation for determining the heating value of a coal.  $82C + aV = \text{heating value}$ , where C stands for the fixed carbon in the coal, V the volatile constituents and  $a$  a variable factor dependent upon the volatile constituents  $V_1$  of the pure (water- and ash-free) combustible. He gave values of  $a$  for all heating substances which in the pure state contain less than 40 per cent. of volatile constituents. Castellana (*Atti accad. lincei* [5], **14**, I, 465) tested for borates and for boric acid by heating the substance with an excess of potassium ethylsulphate till the first vapors come out of the little tube; these burn with a distinct green colored edge to the flame. Testing organic substances like milk he used the calcined residue from 5 to 10 grams. The limit of sensitiveness is 0.5 mg. of boric acid. By careful heating of formic, acetic, butyric, valeric, pelargonic, oxalic, benzoic, salicylic, cinnamic acids and also  $\beta$ -naphthol with potassium

ethyl sulphate the characteristic odors of their esters were obtained. Von Spindler (*Chem. Ztg.* **29**, 582) determined boric acid by acidifying the ash of an organic substance with hydrochloric acid, washing into a flask, making alkaline with sodium hydroxide then adding helianthin and lastly phosphoric acid dropwise till the indicator turned red. The flask had a two-holed rubber stopper through one hole of which was inserted a distillation tube and sidewise bent tube (as in the Kjeldahl) leading to a condenser and through the other a little dropping funnel for the methyl alcohol. The aqueous liquid was distilled off as far as possible, best to dryness, then methyl alcohol was added in 10 cc. amounts, distilling each amount separately till a drop taken from the condenser on a glass rod burned no more with a green flame. Distillation was then carried out once or twice more with 10 cc. amounts of the methyl alcohol. The whole distillate was then treated with a large excess of normal sodium hydroxide, the alcohol boiled off and the liquid evaporated to 20 or 30 cc. After cooling, an equal volume of neutral glycerol was added and the excess of hydroxide titrated back with normal sulphuric acid. Phillips (*Z. angew. Chem.* **18**, 1969) determined silicon and silica together by dissolving the pulverized mixture in hot caustic potash, whereby for one atom of silicon two molecules of hydrogen are liberated, from which it is easy to calculate the silicon. The sum of silicon and silica was obtained by fusing another sample with sodium carbonate and potassium nitrate and the usual silica determination.

*Metals, Alkalies* - Alvarez (*Chem. News*, **91**, 146; *Compt. rend.* **140**, 1186; *Gaz. chim. ital.* **35**, II, 463) recommended a 5 per cent. solution of sodium amino- $\beta$ -naphtholsulphonate, 1, 2, 6-(C<sub>10</sub>H<sub>5</sub>(NH<sub>2</sub>)(OH)<sub>2</sub>(SO<sub>3</sub>Na)<sub>6</sub>, eikonogen) as a test for potassium. The reaction is as delicate as that with chlorplatonic acid. In neutral solutions with potassium salts the corresponding potassium salt of the acid is obtained as brilliant orthorhombic plates, little soluble in water, insoluble in absolute alcohol. The reaction does not take place very rapidly; in 5 to 10 per cent. potassium chloride solution the precipitate forms immediately, in 3 to 5 per cent. solution after ten minutes, in 2 per cent. after a while and in 1 per cent. after a few hours. Klinkerfues (*Chem. Ztg.* **29**, 77, 1085) gave an easy potash determination. He precipitated potassium chlorplatinate, washed it by decantation through a filter with alcohol, dissolved the precipitate in hot water and filtered through the same filter into a weighed platinum dish. The filtrate was treated with a couple of drops of formic acid and evaporated partially to dryness. The platinum was reduced and stuck tightly to the dish. He removed the solution and washed the residue with water or 5 per cent. nitric acid. The dish was then gently ignited and weighed after cooling in a vacuum desiccator.

Novotny (*Z. Elektrochem.*, **2**, 453) determined volumetrically sodium hydroxide in the presence of the carbonate by obtaining first in one portion the total alkalinity with a strong mineral acid and methyl orange, then in another the free alkali after adding barium chloride with oxalic acid and phenolphthalein. The solubility of the barium carbonate might be driven back by a large excess of barium chloride and then even hydrochloric acid could be used for the titration. Reichard (*Chem. Ztg.* **29**, 861) found that hydrofluosilicic acid will precipitate sodium and potassium from most concentrated solutions of salts of the two metals and lithium, leaving the latter in solution. The precipitated sodium and potassium may be determined as usual by conversion into sulphates and determining also the sulphuric acid. With lithium present the precipitation of barium sulphate is valueless because of occlusion. Potassium chlorplatinate he found also to carry down lithium. Grossmann (*Loc. cit.* p. 137) and Rupp (*Loc. cit.* p. 443) preferred the gas volumetric method for the analysis of commercial sodium peroxide to any of the titration methods which all give too low results. Rupp regarded the fact that his titration method does give too low results as proof that the technical product contains higher oxides. Rupp and Rössler (*Arch. Pharm.* **243**, 104) determined ammonium salts by titration with alkali hypobromite (10 grams of NaOH in 500 cc. of water + 17 grams of Br). A suitable volume of the ammonium salt solution was placed in a glass-stoppered vessel and shaken with a known volume of the bromine liquor diluted with water to 50–75 cc. The iodine value of the bromine liquor should be accurately known. After five to ten minutes the liquid was diluted again with 50 cc. of water, acidified with dilute hydrochloric acid and potassium iodide immediately added. The iodine was titrated after about two minutes. There should be half or one-third the original amount of bromine liquor in excess. Free ammonia solutions must be much diluted for the determination. The oxidation was complete when the sample titrated with starch paste did not blue again on standing for a few minutes. One cc. of tenth-normal iodine = 0.0022037 gram of ammonium sulphate, 0.00267 gram of ammonium nitrate, 0.001784 gram of ammonium chloride or 0.0005667 gram of ammonia.

*Alkaline Earths.*—Blum (*Z. anal. Chem.* **44**, 9) observed that a portion of any ammonium sulphide precipitate which does not dissolve in hydrochloric acid should always be tested for barium and strontium sulphates, if it is a question of finding small amounts of these elements. Knett (*Sitzber. Akad. Wiss. Wien*, **113**, 753; *N. Jahrb. Mineral.* 1905, p. 343) reported that the Karlsbad hot springs, though they show no barium on chemical analysis, do in the course of time deposit a very small amount of crystals of barium sulphate which are radioactive. Knett said they

evidently contain radium sulphate and constitute the first uranium- and thorium-free source of radioactive material. De Koninck (*Bull. soc. chim. Belg.*, **19**, 86) found that the limit of sensitivity of the ammonium sulphate precipitation for strontium is 1:20,000 and that strontium and calcium cannot be separated by precipitating strontium with ammonium sulphate and washing with a solution of this salt. He stated further that the solubility of strontium sulphite in the presence of sodium sulphite is about the same as that of strontium sulphate in the presence of ammonium sulphate. Koppeschaar (*Z. anal. Chem.* **44**, 184) gave a new method of determining magnesium carbonate in limestones. He treated 50 grams of the stone with 500 cc. of pure hydrochloric acid (150 cc. of 25 per cent. HCl diluted to 500 cc.), then he added to the solution 50 cc. of concentrated sulphuric acid, cooled and filtered through a porcelain funnel, washing the gypsum left in the beaker on to the filter with the filtrate. The amount of calcium sulphate he obtained by weighing the tared funnel. The filtrate he made ammoniacal, precipitated the calcium still in the solution with 5 grams of ammonium oxalate and precipitated the magnesium in the filtrate with 4 grams of sodium phosphate.  $\text{Mg}_2\text{P}_2\text{O}_7 \times 1.8 = \text{per cent. MgCO}_3$ , in the limestone.

*Iron, Aluminum, Chromium and Rare Earths.*—The brown color (ferrous salt, nitric and sulphuric acids) may be used as a test for ferrous salt in the presence of ferric according to Blum (*Z. anal. Chem.* **44**, 10), by strongly acidifying with sulphuric acid, then adding a crystal of potassium nitrate, when reddish streaks starting from the nitrate will soon show. Divine (*J. Chem. Ind.* **24**, 2) observed that if about 0.10 gram of alumina in solution be treated with 2 cc. of a 25 per cent. solution of tannin then ammonia be added in slight excess, and the solution boiled till the excess is almost gone, the alumina will be precipitated in an easily washed and filtered form. Funk (*Z. angew. Chem.* **18**, 1687) found that on double precipitation with great excess of ammonia and washing with hot 5 per cent. solution of ammonium chloride it was possible to separate iron from zinc. The amount of ammonia should be twenty to thirty times that required for precipitation. He said also that the acetate method is a better one. Giles (*Chem. News*, **92**, 1, 30) found that when a nitric acid solution of the rare earths was treated with lead carbonate in excess thorium, zirconium, trivalent cerium and ferric iron were completely precipitated, tetravalent uranium, trivalent chromium and alumina slowly and incompletely, and ceric cerium and the oxides of lanthanum, neodymium, praseodymium, samarium and the yttrium group not at all. The lead was removed by hydrogen sulphide from the nitric acid solution of the precipitate. Kleine (*Stahl und Eisen*, **25**, 1305) determined chromium and manganese both by titration. Five grams of the steel were dissolved by warming in

50 cc. of hydrochloric acid (sp. gr. 1.12), heated to boiling, 3 cc. of nitric acid (sp. gr. 1.4) added dropwise and the solution evaporated to syrupy thickness. The iron was removed from the cooled solution by means of Rothe's ether-shaking apparatus, then the solution was evaporated to dryness. Ten cc. of sulphuric acid, (1:10) were added, the whole washed into a flask with hot water, boiled for fifteen or twenty minutes after the addition of 150 cc. of ammonium persulphate (60 grams per liter), filtered through an asbestos filter and the precipitate washed with cold water. An excess of ferrous sulphate solution was added to the filtrate and the excess titrated back with permanganate. The same volume of ferrous sulphate solution was titrated with permanganate and the difference gave the amount of iron oxidized by the chromic acid present. The chromium titer of the permanganate is equal to the iron titer multiplied by 0.31. The precipitate of hydrated manganese dioxide with the asbestos filter was treated with 10 cc. of sulphuric acid (1:3) and 10 cc. of oxalic acid (47.5 grams of the acid in two liters of water mixed with 3200 cc. of water and 800 cc. of sulphuric acid), diluted to 200-300 cc. with hot water, shaken up, treated with more oxalic acid, if necessary, and titrated with permanganate. A similar amount of oxalic acid solution was titrated with permanganate and the difference gave the manganese. The manganese titer is equal to the iron titer multiplied by 0.501. Kolb and Ahrle (*Z. angew. Chem.* **18**, 92) found that cinnamic, benzoic, salicylic and especially *m*-nitrobenzoic acid are suited to the separation of thorium from the cerium group earths. Neutral aqueous solutions of a thorium salt give with the latter acid a white flocculent precipitate. If the influence of the free mineral acid be set aside by the addition of aniline *m*-nitrobenzoate the precipitation is complete. Cerous, lanthanum and didymium salts are not precipitated either in hot or cold solution. Ceric salts are precipitated, hence must be reduced by hydrogen sulphide. De Koninck (*Bull. soc. chim. Belg.*, **19**, 181) observed that ferrous and ferric salts give with alkali sulphides a black precipitate of ferrous sulphide while the supernatant liquid has a green or in very dilute solutions a brown tint. The reaction takes place with 0.25 mg. of iron per liter or one part in 4,000,000; it is comparable to the ferrocyanide reaction in delicacy. The change from brown to green is not due to oxidation or reduction nor to formation of double sulphides but probably to a molecular change like that of manganese sulphide (reddish to green), cadmium sulphide (yellow to red), mercury and antimony sulphides (reddish to black). Marre (*Rev. gén. chim. pure et appl.* **8**, 153) recommended the volumetric iron determination proposed in 1904 by Tarugi and Silvatici (ferric solution reddened by potassium sulphocyanate and decolorized by potassium oxalate).



*Manganese, Zinc, Cobalt and Nickel.*—Blum (*Z. anal. Chem.* **44**, 7) observed that barium must be removed with sulphuric acid from manganese ores containing it or else the manganese determination as the sulphide will come out too high because of barium sulphate precipitated by oxidation products of the sulphur of the yellow ammonium sulphide. Gröger (*Chem. Ztg.* **29**, 987) determined manganese in the presence of chromium by a modification of the Volhard method for its determination in the presence of iron. He used an emulsion of zinc sulphate, basic zinc sulphate in zinc sulphate solution (288 grams of pure crystallized zinc sulphate in solution mixed with 28 grams of caustic potash, in 500 cc. of water, kept in a closed flask and shaken before using). He added this to the manganese chromium mixture in a 250 cc. flask on a boiling water-bath till the precipitate was no longer green but gray-violet, cooled, filled to the mark, shook up and filtered. Fifty cc. of the filtrate were boiled with a solution of 20 grams of pure crystallized zinc sulphate in 150 cc. of water and titrated with tenth-normal permanganate to redness. In the presence of larger amounts of chromium than 0.1 gram he used a larger flask than 250 cc. Nissenson and Kettembeil (*Chem. Ztg.* **29**, 951), in work done at the instance of the International Committee, compared the methods of zinc determination and decided that the electrolytic, Schaffner's sodium sulphide and the ferrocyanide methods give equally good results. Hattensaur (*Loc. cit.* p. 1037) criticized Nissenson and Kettembeil for overlooking Schneider's method. Pozzi-Éscot (*Ann. chim. anal. appl.* **10**, 147) added to a very dilute cobalt solution a few drops of an alcoholic solution of phenyl- or phenylnaphthylthiohydrantoic acid and a drop of ammonia. An immediate crimson color appeared. In more concentrated solutions a reddish brown precipitate was obtained. Nickel gave an ochre-yellow color or a dirty gray precipitate which concealed the cobalt reaction, but the nickel compound dissolved in excess of ammonia while the cobalt came out more sharply. Rubricius (*Stahl und Eisen*, **25**, 890) described a persulphate method of determining manganese in iron and steel. The steel turnings (0.25 gram) were dissolved in nitric acid (sp. gr. 1.2) and concentrated over the open fire to about half the volume of the solution, treated with 10 cc. of tenth-normal silver nitrate solution, diluted to about 300 cc., boiled and treated with 10 cc. of a 10 per cent. solution of ammonium persulphate. The well-cooled solution containing all manganese as permanganate was titrated with a solution of 3 grams of arsenious acid and 9 grams of alkali bicarbonate in six liters of water to the green color. Kunze (*Chem. Ztg.* **29**, 1017) described a method similar to this one of Rubricius. Skrabal (*Z. Elektrochem.* **11**, 653) stated that there is an intermediate labile product, the manganic salts, in the oxidation of oxalic acid by permanganate and that the

manganous salt added acts as an inductor, forming manganic salts with the permanganate and the oxalic acid reduces this. Tschugaew (*Ber.* 38, 2520) gave a test for nickel. The liquid to be tested was made strongly alkaline and shaken several times to convert cobalt salts into complex cobaltic compounds, then powdered  $\alpha$ -dimethylglyoxime ( $\text{CH}_3\text{C}(\text{:N.OH})\text{C}(\text{:N.OH})\text{CH}_3$ ) was added and heated to boiling. If the nickel solution was not too dilute, a scarlet precipitate was obtained, with smaller amounts a red scum and with traces the yellow solution deposited a reddish precipitate, recrystallizable from chloroform and alcohol. The compound is  $\text{CH}_3\text{C} \text{---} \text{C} \text{CH}_3 \cdot \text{C}_4\text{H}_8\text{O}_2\text{N}_2$ . The reaction



shows plainly 0.1 mg. of nickel in the presence of 500 mg. of cobalt. The delicacy for pure or cobalt-free nickel solutions is greater than 1:400,000.

*Silver, Lead and Mercury.*—Dittrich and Reise (*Ber.* 38, 1829) gave a determination of lead, using persulphate in acid solution. They added to lead nitrate solution a 10 per cent. solution of ammonium persulphate and obtained white crystalline lead sulphate, which on standing or warming in the persulphate liquid changed incompletely into lead dioxide. The precipitation was ended in five hours, the precipitate being filtered and washed with a solution of ammonium sulphate. After being burned the residue changed quantitatively into lead sulphate on the addition of a few drops of sulphuric acid. Ebler (*Z. anorg. Chem.* 47, 377) gave a gasometric and titrimetric method of determining mercury with hydrazine salts.  $2\text{HgCl}_2 + \text{N}_2\text{H}_4 = 4\text{HCl} + 2\text{Hg} + \text{N}_2$ . This reaction takes place in the presence of sodium acetate. The nitrogen may be measured in a Schiff nitrometer. The method may be used for hydrazine as well. In ammoniacal solution the separation of nitrogen by hydrazine is also quantitative, mercury being reduced to the metal. Instead of measuring the nitrogen the excess of hydrazine can be titrated with iodine solution in the presence of primary potassium carbonate. Silver and copper must be previously removed. L. and J. Gadais (*Ann. chim. anal. appl.* 10, 98) detected lead in tartar as follows: The hydrochloric acid solution, to which was added 0.15 gram of copper as the nitrate was precipitated with hydrogen sulphide, filtered after standing twelve to twenty-four hours, dissolved in nitric acid, filtered and electrolyzed in platinum. Lead will give on the addition of three to four drops of tetramethyldiaminodiphenylmethane an intense blue color, by which 0.1 mg. of lead as the dioxide may be recognized. Lidholm (*Ber.* 38, 566) separated silver and lead by dissolving the alloy or mineral, finally adding tartaric acid, filtering, neutralizing the filtrate, treating with sodium acetate (dissolving the precipitated basic lead acetate in

acetic acid), boiling and treating with 2 cc. of a 4 per cent. solution of hydroquinol for each 0.1 gram of silver. Silver is precipitated and is washed as usual with 5 per cent. ammonium nitrate. Rupp (*Arch. Pharm.* **243**, 300) gave a titrimetric method for determining mercury. He made a few cubic centimeters of a 35 per cent. solution of formaldehyde alkaline, decomposed it with a suitable volume of the mercury solution, warmed for ten or fifteen minutes on the water-bath, allowed to cool and acidified with much acetic acid. He then added tenth-normal iodine solution in excess, shook gently for five minutes, keeping well closed, then titrated the iodine excess with thiosulphate in the presence of starch. One cc. of iodine solution = 0.01002 gram of mercury or 0.01355 gram of mercuric chloride. Utz (*Pharm. Post*, **38**, 491) said Rupp's method could be used for the determination of sublimate in dressings.

*Copper, Cadmium and Bismuth.*—Ebert (*Apoth. Ztg.* **20**, 908) gave a test for very small amounts of copper. A mineral water showing no copper with hydrogen sulphide, potassium ferrocyanide, etc., colored some wadding through which it was filtered pale green. If water made slightly alkaline (one or two drops for 500 cc.) be filtered three times through a funnel provided with a bunch of wadding and the latter remains colorless, there is no copper in the water. Ebler (*Z. anorg. Chem.* **47**, 371) determined copper with hydrazine salts.  $4\text{Cu}(\text{NH}_3)_4\text{SO}_4 + (\text{NH}_2)_2\text{H}_2\text{SO}_4 = 2\text{Cu}_2(\text{NH}_3)_4\text{SO}_4 + \text{N}_2 + 2\text{NH}_3 + 3(\text{NH}_4)_2\text{SO}_4$ . The blue cupric salt goes over into colorless cuprous salt and all the nitrogen of the hydrazine is set free (see Rimini, under "Gas Analysis"). He used a Hempel nitrometer, but drove the gas over by slow distillation and collected over mercury. De Koninck (*Bull. soc. chim. Belg.*, **19**, 91) recommended Cloud's colorimetric determination of bismuth (varying color of lead iodide containing bismuth), stating that amounts of bismuth as low as 0.02–0.03 mg. per 100 cc. of solution could be detected with certainty. Meerburg and Filippo (*Chem. Weekblad*, **2**, 641) stated that 0.0001 mg. of copper might be detected by adding to the hydrochloric acid solution of the copper salt cesium chloride. With little of the latter, red crystals of perhaps  $\text{CuCl}_2 \cdot \text{CsCl}$  are formed. With more cesium chloride yellow crystals of perhaps  $\text{CuCl}_2 \cdot 2\text{CsCl}$  are formed, which turn red on the addition of small amounts of cupric chloride. Cobalt and iron interfere but lead and bismuth do not. Sal-kowski (*Ber.* **38**, 3943) commended, and Staehler and Scharfenberg (*Loc. cit.* p. 3862) gave some details of the quantitative determination of bismuth as the phosphate and its separation from the other heavy metals, especially copper, cadmium, mercury and silver. Bismuth phosphate is insoluble in dilute nitric acid. Ten to 20 cc. of a solution of bismuth in concentrated nitric acid are diluted with 300–400 cc. of water. To the boiling

solution is added dropwise the necessary amount of boiling 10 per cent. sodium phosphate (tertiary) with stirring. If the solution should become alkaline, it is acidified with a little nitric acid. The whole is boiled for a while, allowed to settle, filtered hot and the precipitate washed with hot 1 per cent. nitric acid containing a trace of ammonium nitrate. The precipitate is then dried at  $120^{\circ}$ , ignited for fifteen or twenty minutes over a large Bunsen burner and weighed as  $\text{BiPO}_4$ . The other metals named are left in the filtrate.

*Molybdenum, Vanadium, Tin, Etc.*—Blum (*Z. anal. Chem.* **44**, 2) gave a test for stannous tin depending on his test for ferrous iron. If a stannous solution containing hydrochloric acid be treated with a few drops of ferric chloride solution, ferrous chloride corresponding in amount to the stannous compound is obtained. The ferrous chloride can then be detected by treatment with sulphuric acid and the potassium nitrate crystal. The hydrochloric acid should be driven off by heat before the nitrate crystal is added. Glasmann (*Ber.* **38**, 193) gave an iodometric method of determining the alkali heptamolybdates. An aqueous solution of ammonium heptamolybdate liberates iodine from the potassium iodide-potassium iodate mixture, because the salt hydrolyzes to free molybdic acid and neutral molybdate and the free acid acts in the known way with the mixed iodine compounds. He further (*Loc. cit.* p. 600) gave an oxidimetric method for the determination of molybdic and vanadic acids together. Vanadic acid is reduced in sulphuric acid solution by zinc to  $\text{V}_2\text{O}_2$ , by magnesium to  $\text{V}_2\text{O}_3$ . Molybdic acid gives with each metal in the presence of air  $\text{Mo}_2\text{O}_3$ . If then aliquot portions of the solution be reduced with zinc and acid and magnesium and acid and both reduced solutions be titrated with permanganate (and manganese sulphate) enough data may be obtained so that both acids can be calculated. Von Knorre (*Loc. cit.* p. 783) determined tungsten in the following manner: He added to the cold tungstic acid solution some dilute sulphuric acid or alkali sulphate and then precipitated with a solution of benzidine hydrochloride. The crystalline benzidine sulphate surrounds the benzidine tungstate so well that though the latter filters poorly by itself it can be easily filtered after five minutes and ignited in platinum while still moist to  $\text{WO}_3$ . Melikow and Jeltschaninow (*J. russ. physik.-chem. Ges.* **37**, 99) observed that potassium fluorpercolumbate is colored yellow by hydrogen peroxide in small amounts in the presence of sulphuric acid and that concentrated solutions of potassium per-columbate are colored yellow by concentrated sulphuric acid. One-tenth per cent. of columbium in tantalum preparations can be detected by the help of these reactions. Puschin and Trechinsky (*Loc. cit.* p. 828) separated tin from cobalt and nickel by making use of the fact that tin will come out of an acid solution

of tin ammonium oxalate on electrolysis while cobalt and nickel come out of neutral solution. Nickel or cobalt oxalate precipitates in the liquid, but the electrolysis of the tin salt is carried out and then the nickel or cobalt salt is dissolved by the addition of ammonia and warming. Antimony in nitric acid solution may be separated from copper by a proper regulation of the voltage, which must be at least 2.05 for antimony. Truchot (*Ann. chim. anal. appl.* **10**, 254) observed that heating molybdic acid on porcelain with concentrated sulphuric acid almost to the disappearance of fumes of the latter, cooling and breathing repeatedly on the dish causes a magnificent blue color. With vanadium present the color is green because of the mixture of yellow and blue.

*Platinum Group and Gold.*—Alvarez (*Chem. News*, **91**, 172; *Gaz. chim. ital.* **35**, II, 421; *Compt. rend.* **140**, 1254) gave a new iodine compound of osmium which can be used as a test for the latter. To 2 cc. of aqueous 1 per cent. potassium iodide solution 20 cc. of pure concentrated hydrochloric acid (22° Bé.) or better of phosphoric acid (sp. gr. 1.7) are added, then a drop of the osmic acid solution. The green color may be shaken out with ether.  $\text{OsO}_4 + \text{IOHI} = \text{OsI}_2 \cdot 2\text{HI} + 4\text{H}_2\text{O} + 3\text{I}_2$ . The compound is soluble in water and ether, but insoluble in benzoic acid and chloroform. As a test for rhodium the same author (*Loc. cit.* **91**, 216; **35**, II, 431; **140**, 1341) recommended the blue liquid formed when the green  $\text{Rh}(\text{OH})_4$  is oxidized in alkaline solution by chlorine or hypochlorite. A rhodium salt solution treated with an excess of sodium hydroxide and chlorine passed in turns reddish yellow, intense red, then becomes cloudy, a fine green precipitate comes out and this finally dissolves, forming a blue solution like ammoniacal copper; the color is that of Claus's sodium perrhodate,  $\text{Na}_2\text{RhO}_4$ . Nordenskjöld (*Svensk Kemisk Tidskrift*, 1905, 54; through *Pharm. Ztg.* **50**, 633) gave a technical determination of the platinum metals. Iridium and rhodium do not dissolve in aqua regia and osmium is oxidized by concentrated aqua regia to osmic acid which can be separated by its volatility. Palladium, soluble in other acids, is separated first. The dilute platinum solution is precipitated with metallic magnesium, warmed for a quarter of an hour on the water-bath, filtered, washed, ignited gently, washed again after moistening with hydrochloric acid, ignited in a current of hydrogen, allowed to cool in carbon dioxide and weighed. The precipitate is treated again with dilute aqua regia, the platinum precipitated again with magnesium, washed well, finally acidified with hydrochloric acid, ignited and weighed. Quennessen (*Chem. News*, **92**, 29; *Bull. soc. chim.* [3], **33**, 875) separated platinum and iridium by means of precipitation with magnesium and extracting platinum from the ignited residue with dilute aqua regia.

**Separations.**—Jannasch (*J. pr. Chem.* [2], 72, 35), with Cohen (*Loc. cit.* p. 14), with Rühl (*Loc. cit.* p. 1), with Schilling (*Loc. cit.* p. 26), and with von Mayer (*Ber.* 38, 2129, 2130) gave a number of hydrazine and hydroxylamine separations as aluminum, chromium and iron from copper and zinc, from manganese, magnesium and nickel, of iron and thorium from uranium, and of gold and platinum from other metals. Friedheim (*Z. anal. Chem.* 44, 388), with Jacobius (*Loc. cit.* p. 465) and with Hasenclever (*Loc. cit.* p. 593), attacked the hydrogen peroxide, hydrochloric acid and hydroxylamine separations given in Jannasch's "Praktische Leitfaden der Gewichtsanalyse," saying that many of them would not work and that others were no better than the older methods. Lastly, Donath (*Loc. cit.* p. 698) claimed priority over both Jannasch and Friedheim in the gravimetric determination of manganese by hydrogen peroxide.

#### ANALYSIS OF ORGANIC COMPOUNDS.

**Reagents and Quantitative Determinations.**—Aloy and Laprade (*Bull. soc. chim.* [3], 33, 860) observed that a neutral solution of uranyl nitrate is colored a fine red by phenols. Ten grams of the nitrate were dissolved in 60 cc. of water and dilute ammonia added to beginning cloudiness, then the solution was filtered and the filtrate diluted to 100 cc. The solution to be tested was neutralized and 2 cc. of it treated drop-wise with the reagent till the maximum color was obtained. Mineral acids and alkalis cause the color to disappear. The reaction is in general sharp at dilutions of 1:1000 and visible at 1:10,000. Alvarez (*Chem. News*, 91, 125; *Bull. soc. chim.* [3], 33, 713; *Gaz. chim. ital.* 35, II, 432) used sodium peroxide as a test for the polyphenols, their isomers and higher organic compounds. He mixed 0.2 gram of the peroxide, 0.04–0.05 gram of the polyphenol and 5 cc. of absolute alcohol, then after 4–6 minutes added 15 cc. of water. He obtained:

Substance.	Color in alcohol.	Color in water.
Pyrocatechol.	Flesh, then green and brown.	Reddish brown.
Resorcinol.	Yellow, then greenish.	Darker green.
Hydroquinone.	Reddish yellow.	Orange.
Pyrogallol.	Reddish brown.	Red with yellow borders, after 24 hours orange.
Oxyhydroquinone.	Red-violet shades.	Yellow.
[1,2,4] Phloroglucinol.	Red-violet.	Deeper violet, finally almost colorless.
Orcinol.	Flesh-colored.	Rose-red.
Methylpyrocatechol.	Blue-violet, then red.	Reddish brown with yellow edges.
Thymohydroquinone.	Intense red.	Wine-red, finally colorless.

Guérin (*J. pharm. chim.* [6], 21, 14) gave a list of the color reactions obtained with alcohols (except methyl and ethyl) and with

substances containing the hydroxyl group when treated with 5-6 drops of a saturated aqueous solution of furfurol in the presence of concentrated sulphuric acid. Solid compounds were dissolved in concentrated sulphuric acid. The color was usually some shade of violet. Wechuizen (*Pharm. Weekblad*, **42**, 271) recommended phenolphthalin as a reagent for detecting hydrocyanic acid. Phenolphthalin solution made alkaline with sodium hydroxide and some 1:2000 copper sulphate added, then treated with the hydrocyanic acid solution yields in the cold a red color, the phenolphthalin being oxidized to phenolphthalein. The color is distinctly visible with 1 part of acid in 500,000 of water. Lévy and Pécoul (*Compt. rend.* **140**, 98) modified Gautier's method for the detection of carbon monoxide by reduction of iodic acid at a temperature of 60°-80°. They took up the iodine directly in 3-4 cc. of chloroform protected from the air by a layer of distilled water and then compared the color of the solutions with that of type solutions. With a special apparatus they detected 1 part carbon monoxide in 20,000 in a mass of 4 liters of air, or an amount of illuminating gas no longer detectable by its odor. Stortenbeker (*Rec. trav. chim.* **24**, 66) detected iodoform in meat samples by distillation with steam. The fatty acids passing over with the iodoform were neutralized and the latter extracted with ether. The ether residue recrystallized from acetic acid gave well developed hexagonal crystals easily recognizable under the microscope. Sudborough and Thomas (*Pr. Chem. Soc.* **21**, 88; *J. Chem. Soc.* **87**, 1752) determined acetyl groups by distilling with steam the acetyl derivative (0.5-1.0 gram) added to a 10 per cent. solution of pure benzenesulphonic acid until the distillate ceased to be acid. The distillate was then titrated with barium hydroxide, using phenophthalein as indicator. Naphthalene  $\alpha$ - or  $\beta$ -sulphonic acid could be used instead of benzenesulphonic acid.

*Alcohols and Aldehydes*.—Kahn (*Pharm. Ztg.* **50**, 651) tested for methyl alcohol in liquids containing ethyl alcohol by diluting 0.5-1.0 cc. of the liquid with 10 volumes of water in a test-tube, putting repeatedly into the liquid a glowing copper spiral, adding 5 cc. of milk and a few drops of ferric chloride and allowing this liquid to flow carefully upon a few cc. of concentrated sulphuric acid without mixing. In the presence of methyl alcohol a violet zone at the contact surface between the two liquids was obtained inside of three minutes. Utz (*Pharm. Centrbl.* **46**, 736) gave a test very like this one. Lindet (*Bull. assoc. chim. suc. dist.* **22**, 475) recommended a modification of Eury's test for a rapid detection of formaldehyde in alcohol denaturated with it. He broke up a piece of dry casein in 10 cc. of the alcohol, added a few drops of ferric chloride solution, then 10 cc. of phosphoric acid and 10-15 cc. of sulphuric acid and obtained a violet then a brown color. The delicacy is 1:

300,000. Schuch (*Z. landw. Vers. Wes. Ost.* **8**, 1058) criticized Lindet's test, saying that dilute acetaldehyde, pure water and alcohol will give the reaction. He modified Arnold and Mentzl's test, distilling 10 cc. from 300 cc. of wine with good cooling, then shaking 5 cc. of the distillate with 1.5 cc. of a solution of phenylhydrazine hydrochloride (1:50), adding four drops of ferric chloride and 10-12 of concentrated sulphuric acid. The color is red and the reaction is delicate to 1:200,000. Schulze (*Loc. cit.* p. 155 and *Chem. Ztg.* **29**, 976) and Henkel and Roth (*Z. angew.Chem.* **18**, 1936) made comparative studies of the various methods for the determination of glycerol. Braun (*Chem. Ztg.* **29**, 763) and Strauss (*Loc. cit.* p. 1099) gave modifications of the bichromate method. Shukoff and Schestakoff (*Z. angew. Chem.* **18**, 294) determined glycerol directly by mixing the sample with sodium sulphate dehydrated by ignition and then extracting in a Soxhlet apparatus with dry acetone. The acetone might be subsequently distilled off and the glycerol weighed directly in a closed vessel. The mixture should be made slightly alkaline before extraction with potash. The acetone extraction should last 4 hours and the glycerol should be dried for 4-5 hours at 75°-80° in an air-bath to constant weight. The Dynamitfabrik Schleich (*Loc. cit.* p. 1656) reviewed the above method and recommended a filtration before making the liquid alkaline, also drying for 5-6 hours at 90°-95°. The method gives slightly too high results. Landsberger (*Chem. Rev. Fett.- Harz.- Ind.* **12**, 150) compared the above method with the acetin method of Lewkowitsch and found the results of the two methods to agree generally very well. Nierenstein (*Collegium*, 1905, p. 158) observed that formaldehyde gives a brown-red color with 0.5 per cent. phloroglucinol solution. Seyewitz and Bardin (*Bull. soc. chim.* [3], **33**, 1000) determined acetaldehyde by diluting the solution to be determined to a content of 7-8 per cent., then putting 10 cc. of this solution into 40 cc. of exactly neutralized 10 per cent. sodium sulphite solution and titrating with standard sulphuric acid in the presence of a drop of 2 per cent. alcoholic phenolphthalein. The mixture should be cooled to 4-5°.  $2\text{Na}_2\text{SO}_3 + 2\text{CH}_3\text{CHO} + \text{H}_2\text{SO}_4 = (\text{NaHSO}_3 + \text{CH}_3\text{CHO})_2 + \text{Na}_2\text{SO}_4$ . Voisenet (*Loc. cit.* p. 1198) gave a very delicate test for formaldehyde and for albumens. He poured 2-3 cc. of water over about 0.1 gram of finely powdered egg albumen or put 2-3 cc. of an albumen solution in a test-tube, added a drop of 5 per cent. solution of formaldehyde and diluted with 3 volumes of a strong nitrous acid solution (0.5 cc. HCl of density 1.18 added to 1 liter of a 3.6 per cent. solution of  $\text{KNO}_2$ ). On mixing, a reddish color appeared and after 5 minutes an intense violet-blue. Heating to 50° favored the coloration. No color is obtained without the aldehyde except a weak red one after hours. By use of a weak nitrous



acid solution (0.25 cc. of acid added to the nitrite instead of 0.5 cc.) and by warming to 50° for 20 minutes 1 part aldehyde in 10,000,000 can be detected. The test is more delicate if carried out immediately after addition of the aldehyde but even after 48 hours 1 part in 1,000,000 can be detected. The test may be used for the detection of formaldehyde in foods, etc.

*Ketones and Acids.*—Kutscherow (*Z. anal. Chem.* **44**, 622) stated that 0.3 gram of vanillin in 5 cc. of pure alcohol gives with 1 cc. of sulphuric acid no color or a pale yellow one, depending on the purity of the spirits. If these contain 1 per cent. of ketones intense fine colors are obtained, carmine-red with acetone and blue with the higher ones, sometimes with a shade of green which disappears shortly. The acetone color changes to citron-yellow on dilution with water, the blue of the others decreasing in intensity only as colors do on dilution with an indifferent solvent. The diluted acetone color becomes intense orange-red if the solution be made alkaline with caustic potash or soda, while the other ketone solutions become decolorized or pale yellow. The colors can be used for an approximate determination of the amount of ketones present. Amyl alcohol and furfural do not interfere but aldehydes do. Bodlander (*Z. Elektrochem.* **11**, 185) gave an electrometric determination of carbon dioxide. Water takes up carbon dioxide in proportion to its partial pressure, and a corresponding amount of hydrogen ions are released. The latter is a measure of the carbon dioxide and may be easily determined. For practical purposes the combination  $\text{Ag} \mid \text{AgCl} \mid \text{KCl} + \text{KHCO}_3 + \text{K}_2\text{SO}_4 \mid \text{PtO}_2$  is a good one. The same solution surrounds both electrodes. By use of air containing 0.03 per cent. carbon dioxide, the electromotive force is 0.268 volt. Sulphur dioxide must be removed. Methane in mine gases can thus be determined, converting it into carbon dioxide by burning over hot copper oxide. Croner and Cronheim (*Berl. klin. Wochschr.* **42**, 1080) gave a new test for lactic acid, using the Vournasos principle. A few cc. of the juice suspected to contain lactic acid were diluted with water, made strongly alkaline with 10 per cent. potassium hydroxide, boiled for a few minutes, then treated with an iodine solution (2 grams KI in at most 5 cc.  $\text{H}_2\text{O}$ , 1 gram sublimed I, the solution filtered through glass wool and diluted to 50 cc., then 5 cc. of aniline added, the whole kept in a dark colored bottle). In the presence of lactic acid the unpleasant odor of phenyl isocyanide is obtained. The reaction is delicate to 0.0025 gram of acid in 100 cc. of juice. Rupp (*Arch. Pharm.* **243**, 69) determined formic acid titrimetrically by diluting, in a glass-stoppered flask, a suitable volume of bromine lye (15 grams NaOH, 15 grams Br and  $\text{H}_2\text{O}$  to 500 cc.) of known iodine value to about 70–100 cc. with water, then adding a known amount of the formic acid solution (not more than enough to use up about half of the

bromine). Then he added dilute hydrochloric acid from a burette till the bromine color began to remain, allowed the whole to stand for 30 minutes in the dark, added 1 gram of iodine and 10–20 cc. of hydrochloric acid and titrated with tenth-normal thiosulphate. One cc. thiosulphate = 0.0023 gram of formic acid.

*Cyanogen Compounds.*—Astruc and Pegurier (*Ann. chim. anal. appl.* 10, 302) used Lemaire's principle of precipitation with picric acid for the removal of antipyrine in the determination of pyrimidone. They dissolved 0.231 gram of pyrimidone in 10 cc. of water, precipitated by means of 40 cc. of twentieth-normal picric acid, shook for a few minutes and titrated back 25 cc. of the filtrate with twentieth-normal alkali and phenolphthalein. The pyrimidone content =  $(40 - 4n) \times 5$  if  $n$  = the number of cc. of alkali. Pegurier (*Loc. cit.* p. 392) found also that antipyrine behaves toward helianthine as a neutral substance while pyrimidone acts like a monobasic one. He therefore recommended the solution of 0.231 gram of the sample in 10 cc. of water, neutralizing exactly with tenth-normal acid and then carrying out the titration with picric acid. Bourcet (*Bull. soc. chim.* [3], 33, 572) gave a test for antipyrine in the presence of pyrimidone. He dissolved 1–2 grams of the sample in 4–5 cc. of cold water, added then 2 drops of concentrated sulphuric acid and 2 drops of a saturated sodium nitrite solution and shook the mixture. Pure pyrimidone gives first a blue-violet color, becoming later colorless, especially with excess of nitrite. With antipyrine present a blue-violet color is also first obtained which becomes, with more nitrite, a stable green-blue. One per cent. of antipyrine can be detected with certainty. Patein (*J. pharm. chim.* [6], 22, 5; *Bull. soc. chim.* [3], 33, 845) gave a test likewise for these two substances, depending on the fact that antipyrine forms with formaldehyde in the presence of hydrochloric acid diantipyrinemethane while pyrimidone remains unchanged. One gram of the pyrimidone in 5 cc. of water is treated with 5 cc. of water, then 2 cc. of 40 per cent. formaldehyde and allowed to stand 4 days at ordinary temperatures or heated for 4 hours on the water-bath, diluted with 10 cc. of water and made alkaline with ammonia. Without antipyrine the liquid remains clear, but with it insoluble diantipyrinemethane is obtained. Guérin (*J. pharm. chim.* [6], 22, 433) modified the methods of Liebig and of Fordos and Gélis for the volumetric determination of free hydrocyanic acid in aqueous solutions, adding borax to the acid solution before titration with silver nitrate or with iodine. 10 cc. of dilute acid solution are treated with 10 cc. of 3 per cent. borax solution and titrated with 3.148 per cent. silver nitrate or with 9.407 per cent. iodine solution to the appearance of a permanent cloud or to a yellow color. 1 cc.  $\text{AgNO}_3$  = 1 cc.  $\text{I} = 0.001$  gram  $\text{HCN}$ .  $2\text{HCN} + \text{Na}_2\text{B}_4\text{O}_7 = \text{H}_2\text{B}_4\text{O}_7 + 2\text{NaCN}$ .

$2 \text{NACN} + \text{AgNO}_3 = (\text{AgCN} \cdot \text{NaCN}) + \text{NaNO}_3$ .  $\text{AgCN} \cdot \text{NaCN} + \text{AgNO}_3 = 2\text{AgCN} + \text{NaNO}_3$ .  $2\text{HCN} + 2\text{I}_2 = 2\text{ICN} + 2\text{HI}$ .  $2\text{HI} + \text{Na}_2\text{B}_4\text{O}_7 = \text{H}_2\text{B}_4\text{O}_7 + 2\text{NaI}$ . Von Mahler (*Chem. Ztg.* **29**, 32) gave a qualitative test for saccharin. He evaporated the ether solution of the substance to be tested, put the dry residue into a little tube sealed at one end and containing already a piece of sodium or potassium, warmed and threw the yet hot tube into a beaker of freshly prepared sodium nitroprusside solution. The resulting test for sulphur compounds is proof of saccharin under these conditions. Procter (*Pr. Chem. Soc.* **21**, 62; *J. Chem. Soc.* **87**, 242) gave a quantitative determination of saccharin. One-half to 1 gram of the powdered substance was put into a 200 cc. glass-stoppered flask with 50-75 cc. of freshly boiled distilled water, 1-2 crystals of potassium iodide added, then 10 cc. of 5 per cent. potassium iodate solution and the whole shaken. The orthobenzoic acid sulphinide dissolves immediately, liberating an equivalent amount of iodine which is titrated with tenth-normal thiosulphate. The parasulphaminobenzoic acid dissolves more slowly. 1 cc. tenth-normal thiosulphate = 0.0183 gram saccharin. To determine both constituents he made the total titration and also determined the ammonia formed by boiling the sample with 100-fold the quantity of normal hydrochloric acid. The number of cc. of tenth-normal acid corresponding to this ammonia subtracted from the number of cc. of tenth-normal thiosulphate of the total titration and the difference multiplied by 0.0201 gives the amount in grams of the para compound. Leuba (*Ann. chim. anal. appl.* **10**, 218) determined copper ferrocyanide by boiling with 5 per cent. oxalic acid for two hours with a return-flow condenser, filtering and washing the green-yellow precipitate, dissolving it in nitric acid and adding this solution to the filtrate, in which copper and iron were determined as usual.  $\text{Cu}_2\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{C}_2\text{O}_4 = 2\text{CuC}_2\text{O}_4 + \text{FeC}_2\text{O}_4 + 6\text{HCN}$ . Rupp (*Arch. pharm.* **243**, 458) gave a method for the titrimetric determination of cyanides, sulphocyanates and chlorides. Cyanides are oxidized in alkaline solution by iodine to cyanates.  $2\text{NaOH} + \text{I}_2 = \text{NaIO} + \text{NaI} + \text{H}_2\text{O}$ .  $\text{NaIO} + \text{CN}' = \text{NaI} + \text{CNO}'$ . 10 cc. of about 4 per cent. potassium cyanide solution were mixed with 5-20 cc. of normal potassium hydroxide in a flask and 25 cc. of tenth-normal iodine solution added with shaking, the whole diluted after standing to 100 cc., acidified with dilute hydrochloric acid and the precipitated iodine titrated with tenth-normal thiosulphate. Sulphocyanates may be titrated in the same manner. 1 cc. thiosulphate = 3.25 mg. KCN = 1.2125 mg. KCNS. Cyanides in bicarbonate alkaline solution behave thus:  $\text{CN}' + \text{I}_2 = \text{ICN} + \text{I}'$ . On acidification, the reaction may be expressed thus:  $\text{ICN} + \text{HI} = \text{HCN} + \text{I}_2$ . No iodine is therefore used. Sulphocyanates under the same condi-

tions give  $\text{CNS}' + 8\text{I} = \text{CNI} + \text{SO}_3 + 7\text{I}$ , and on acidification  $\text{ICN} + \text{HI} = \text{HCN} + \text{I}_2$ . Hence 6 atoms of iodine are used. Therefore, in a mixture of cyanide and sulphocyanate the latter is easily determined. With chlorides also present all three are determined as silver salts, then in one portion cyanide and sulphocyanate are titrated and finally sulphocyanate alone in another.

*Carbohydrates.*—Ewers (*Z. offentl. Chem.* **11**, 374) concluded that direct polarization should not be used as a basis for the detection of starch sugar in fruit juices because of its great variations and that in its place total sugar should be determined. He would test the fruit juice for invert sugar. If over 2 per cent. is found he would determine the total sugar gravimetrically. The presence of starch sugar may be accepted when for 100 per cent. sugar calculated as cane-sugar the levorotation of the invert solution of 26 grams of syrup in 100 cc. of water in a 200 mm. tube polarizes  $28^\circ$  or less. De Graaf (*Pharm. Weekblad*, **42**, 685) found that free diphenylhydrazine boiled with lactose and 2–3 drops of acetic acid gave a yellow-red, then brown-red, dark black-green and finally brown liquid. If 70 per cent. alcohol was added after the green color appeared a characteristic green liquid was obtained. The green color was soluble also in amyl alcohol, chloroform and ether but not in water or carbon bisulphide. Glucose and saccharose gave only the brown-red color. Hoglund (*Z. Ver. Rubenzuck.-Ind.* 1905, p. 1048) found that cellulose (of filter-paper or of the beet itself) caused a loss of sugar by absorption in the polarization of alcoholic sugar solutions. Kopecky (*Collegium*, 1905, p. 150) detected cellulose in hide powder by moistening 0.2–0.3 gram of the latter with a solution of iodine and zinc chloride (6 grams KI + 100 grams  $\text{ZnCl}_2$  of density 1.80 saturated with I) and after 2–3 minutes adding 25 cc. of water and shaking. On a white background the deep violet cellulose is to be distinguished easily from the yellow hide substance. Lavalley (*Ber.* **38**, 2170; *Chem. News*, **91**, 299) modified the Fehling method of determining sugar by heating 5 or 10 cc. of Fehling solution with 30 cc. of sodium hydroxide (1:3) and 50 or 60 cc. of water to beginning boiling in a 200 cc. dish and then gradually adding the sugar. The operation is ended with the disappearance of the blue color; the cuprous oxide does not precipitate. This method was recommended by Sidersky (*Bull. assoc. chim. suc. dist.* **23**, 426). Ling and Rendle (*Analyst*, **30**, 182) determined the end point of the cuprous oxide precipitation by the use of ferrous sulphocyanate. They dissolved 1 gram of ferrous ammonium sulphate and 1 gram of ammonium sulphocyanate in 10 cc. of water at  $45^\circ$ – $50^\circ$ , cooled and added 50 cc. of concentrated hydrochloric acid. The brownish red color was removed with a little zinc dust and a later red in the same way. The reagent became

instantly red on the addition of copper sulphate and 2 cc. of Fehling solution in a liter could be detected with it. Wolff (*Ann. chim. anal. appl.* **10**, 427) observed that the cuprous oxide obtained in the ordinary way may be treated with ferric sulphate in sulphuric acid solution and the ferrous sulphate formed titrated with permanganate. Another modification of the Fehling method for small amounts of sugar was given by Bilinski (*Pharm. Post*, **38**, 85, 98; *Monatsh.* **26**, 133). Fifty cc. of urine were treated with uranyl nitrate (4:100) till a drop of the mixture colored powdered potassium ferrocyanide brown-red. The urine was added to a definite quantity of the Fehling solution so as to have all the copper reduced. When it was reduced the slightest excess of sugar would reduce also the uranium, giving the precipitated cuprous oxide a green or brownish color. Luhrig (*Pharm. cenrh.* **46**, 951) found that there was considerable error in the use of animal charcoal in the methods for the determination of starch syrup, because of its absorptive power. It causes an error of as much as 10 per cent. of starch sugar in the official methods. The method of Juckenack for the investigation of fruit juices contains this error. Rank (*Z. Osterr. Apoth.-Ver.* **43**, 1038) determined sugar in urine by decomposing 2-3 cc. of the latter with the same volume of potassium hydroxide solution, adding 0.1-0.2 gram of phenylhydrazine and boiling until solution was effected. On slow acidification with dilute acetic acid the solution became cloudy if sugar was present. The test was even more certain if the urine were clarified with lead acetate and the test carried out on the filtrate. One-tenth per cent. of sugar or less could be detected.

*Alkaloids*.—Alverez (*Chem. News*, **91**, 179; *Compt. rend.* **140**, 1540; *Gaz. chim. ital.* **35**, II, 429) gave a new reagent for aconitine. The alkaloid (0.0005-0.0002 gram) was treated with 5-10 drops of bromine, warmed somewhat in a salt-water bath, then 1-2 cc. of fuming nitric acid added and evaporated in the same bath with the addition of some more bromine, when the acids lose their color and a yellow oxidation product is formed. Then 0.5-1.0 cc. of a saturated solution of caustic potash in alcohol (made from pure alcohol of density 0.796) was added, evaporated to dryness, giving a red-brown mass, allowed to cool and 5-6 drops of a 10 per cent. aqueous copper sulphate solution added, giving a deep green color. Reichard's (*Pharm. Centr.* **46**, 252, 309, 385, 479, 644, 846, 935 and *Pharm. Ztg.* **50**, 314, 430, 877) series of articles on the reactions of nicotine, coniine, quinine, cinchonine, aconitine, sparteine, veratrine, caffeine, theobromine, quinidine, cinchonidine and piperine is worthy of note again as last year.

*Coloring Materials and Oils*.—Knecht (*J. Soc. Dyers Colorists*, **21**; *Chem. Centr.* 1905, I, p. 777) determined methylene blue by reduction with titanium trichloride. One gram of the

blue was dissolved in 250 cc. of water, 50 cc. of the solution put into a conical flask and warmed after the addition of a little hydrochloric acid. Carbon dioxide was then passed into the flask and its contents were titrated with titanium trichloride solution to decolorization. A similar method he applied to other coloring-materials reducible by the trichloride. Majstorovic (*Chem.-Ztg.* 29, 309) found that in the mean a rise of temperature of  $0.5^{\circ}$  in the flashing point of petroleum indicated a vapor loss of 0.113 per cent. from a closed reservoir of 1,000,000 kg. content. He thinks it possible to determine the amount of loss by evaporation in this way. Budde (*Veröffentl. aus dem Gebiete des Militär-Sanitätswesens*, 1905, No 29; *Pharm. Ztg.* 50, 432; *Apoth. Ztg.* 20, 421) determined pure rubber in rubber goods by pouring over 1 gram of the sample in a 100 cc. measuring flask carbon tetrachloride, allowing to stand till division of particles or solution had taken place, filling to the mark and filtering through glass wool 10 cc. for analysis. This he diluted to 50 cc. with carbon tetrachloride, and added 50 cc. of a brominating liquid (16 grams  $\text{Br} + 1$  gram  $\text{I}$  dissolved in  $\text{CCl}_4$  to 1000 cc.), obtaining after a time a precipitate. As soon as the supernatant liquid was clear he added 50 cc. of absolute alcohol. The tetrabromide of rubber was brought on to a filter (dried previously at  $50^{\circ}$ – $60^{\circ}$  and weighed), washed first with a mixture of 2 parts carbon tetrachloride and 1 part alcohol, then with pure alcohol and dried at a temperature not exceeding  $60^{\circ}$ . 456 grams of this compound correspond to 136 of pure rubber. Torrey (*India Rubber J.* 30, 417, 467) gave a new method for the determination of rubber based on the color reaction caused by treating the rubber with concentrated nitric acid and then rendering alkaline. The color is deep red. Ditmar (*Gummiztg.* 20, 204) said Torrey's method has no scientific foundation, that rubber breaks up in a complex way and that the one coloring-matter,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$ , is only a small part of the resulting products, oxalic acid and a second coloring body being among the others. Further, the ratio of these products is not constant.

*Milk.*—Bellier (*Ann. chimanal. appl.* 10, 268) gave a new method of milk analysis. Prismatic pieces of poor quality sponge of about 0.2 gram weight were pressed out with very dilute hydrochloric acid till no more sand appeared, then washed with alcohol, ether and finally water. One was dried at  $80^{\circ}$  and weighed with a similarly dried filter, then 5 cc. of milk was completely soaked up into it. The sponge hung on a thread, was dried at  $80^{\circ}$ , put into the filter and weighed after cooling. The increase in weight multiplied by 20 gives the grams of extract in 100 cc. of milk. The sponge was then extracted in a Soxhlet apparatus with water-free ether, the fat being removed by the fifth siphonation. The sponge was weighed after drying and cooling

and the fat obtained by difference. The albumens were rendered insoluble by exposing the sponge to the vapor from a gently boiling formaldehyde solution. The sponge was then allowed to stand for a quarter of an hour in 50 per cent. alcohol containing 5 per cent. acetic acid, then it was hung in water, changing the water five times. In the sponge were left only the albumens and at most 0.01 gram of mineral matter calculated to 100 cc. of milk. The difference between its weight at this point and the preceding weight multiplied by 20 gives the amount of milk-sugar and ash and 0.01 gram. The difference between the last weight and the original weight multiplied by 20 gives the amount of albumen in 100 cc. of milk and 0.01 gram mineral matter, which may be taken as constant. The ash was determined directly in 10 cc. of milk by ignition, and may be assumed for rapid work to be constant at 0.7 gram per 100 cc. for unadulterated cow's milk. Bordas and Touplain (*Compt. rend.* 140, 1099) gave also a new rapid method. Ten cc. of milk were allowed to drop into the tared tube of a centrifugal machine, in which there was 65 per cent. alcohol acidified with acetic acid, allowed to settle for a moment, whirled, decanted, stirred again with 30 cc. of 50 per cent. alcohol, decanted again and the lactose determined in the combined liquids by Fehling's solution. The milk residue was extracted twice, adding first each time 2 cc. of 96 per cent. alcohol, then 30 cc. of ether and whirling each time for a few minutes. The ethereal extract was evaporated in a tared vessel and the butter weighed after drying. The casein remains in the tube of the machine as a fine powder and is dried at a low temperature and weighed. The ash was determined in 10 cc. of the milk by ignition. Dekker (*Pharm. Weekblad*, 42, 977, 1002) determined fat in milk by boiling 10 cc. of the sample with 10 cc. of concentrated hydrochloric acid in a flask until the casein had, to some extent, disappeared, shaking after cooling with 50 cc. of chloroform, adding after 5 minutes 3 grams of tragacanth and shaking again. Forty cc. of chloroform could be poured off the slime and this contained the fat of 8 cc. of milk. The chloroform was distilled off, the fat dried for an hour and weighed. Morres (*Milch-Ztg.* 34, 573, 585) recommended the alcohol test as of most value in determining the keeping quality of milk. He added 2 cc. of milk to 2 cc. of alcohol (68 per cent. by volume). The size of the flakes is a measure of the readiness of the milk to curdle, sour milk yielding great flakes. With alcohol 4 degrees of acidity can be detected as against 5.5 by heating. Utz (*Chem. Ztg.* 29, 669) gave a new test for formalin in milk. Milk and hydrochloric acid (density 1.19) treated with a few grams of vanillin gives a violet-red color, but if formalin is present the liquid is colored yellow. Piperonal and paraoxybenzaldehyde give similar reactions but not so delicate.

*Butter and Blood.*—Soltzien (*Pharm. Ztg.* 50, 398 and *Chem.*

*Rev. Fett.-Harz-Ind.* **12**, 125) used acetone to determine fat, water and non-fat in butter and cream. Five grams of cream were put into a glass-stoppered, weighed Erlenmeyer flask containing a few pieces of pumice with 100 cc. of a mixture of 1 volume of acetone and 1.5 volumes of absolute ether and shaken hard for half a minute. The flask was cooled, the stopper washed with the acetone mixture and the contents of the flask heated to beginning boiling with a return-flow condenser. After cooling, the liquid was poured through a weighed filter into a weighed distilling flask (about 300 cc. size) containing a few pieces of pumice. The residue in the Erlenmeyer flask was weighed 3 times with 20 cc. each time of the acetone mixture, with a little warming, finally with absolute ether, pouring the washings through the filter. In the filtrate the fat was determined by evaporation of the solvent and weighing of the residue. The Erlenmeyer flask and the filter were dried to constant weight for the non-fat. One hundred per cent.—(per cent. fat + per cent. non-fat) = per cent. water. With butter 10 grams were used. Bence (*Centr. Physiol.* **19**, 198) gave a new method for determining the volume of the blood corpuscles in small masses of blood. He added to 100 parts of blood a known amount of 0.9 per cent. sodium chloride solution and gave the following equations:  $S(R - 1.3328) + K(1.3342 - 1.3328) = S + K(R_x - 1.3328)$  or  $S = K(R_1 - 1.3342)(R - R_1)$ , where  $S$  = amount of serum,  $R$  = its refractive index,  $K$  = amount of sodium chloride solution of refractive index 1.3342 if that of water is 1.3328. The refractive index  $R_1$  of the mixture of  $S$  and  $K$  lies between 1.3342 and  $R$ . With  $R$ ,  $K$  and  $R_x$  known,  $S$  can be calculated. Koeppe (*Pflüger's Arch.* **170**, 187) determined the volume of the blood corpuscles by centrifuging the blood in graduated oil pipettes at 5000 or more revolutions per minute.

A portion of the work for this review was done in the library of the department of chemistry of Cornell University, through the courtesy of Professor L. M. Dennis, for which the writer desires to express his thanks.

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## NEW BOOKS.

GESAMMELTE WERKE. By ADOLF VON BAEYER. Vol. I, 990 pp., with an introduction, 132 pp. Vol. II, 1194 pp. Braunschweig: Vieweg und Sohn. 1905. Price, bound, 20 marks.

It is almost with a feeling of reverence that I attempt to give the readers of the *Journal* a brief outline of the colossal work of one of the greatest chemists of the age, Adolf von Baeyer. I am at a loss even in summarizing these two great volumes, for an



enumeration of his papers alone would occupy more space than could be given to this review. All that I can hope to do is to give the reader a glance at the man himself and to mention a few of his greatest discoveries.

In reading this great work, compiled and published by his students and friends in commemoration of his seventieth birthday, one can not help wishing that the author had given more of his biography, notwithstanding the fact that the volumes are in no way biographical. In his very brief "Erinnerungen," however, one gets a flash-light picture not only of Baeyer the boy, the student, the scientist, the man, but also new perspectives of some of his famous co-workers and pupils. Boyhood, as such, was evidently cut out of his life, for we find him at the age of nine delving into chemical problems worthy of the greatest chemists of the time. He was but nine years old when he made his first chemical discovery in the double salt of copper and sodium carbonate,  $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$ . John Stuart Mills had mastered the principles of logic and calculus at the age of ten. Baeyer had done more than this at the age of nine.

His life work has been almost wholly organic chemistry. The greater part of his work has been on the following subjects:

The Indigo Group and Indigo Synthesis.

The Uric Acid Group.

Pyrrol and the Pyridine Bases.

The Phthaleines.

The Hydro-aromatic Compounds, Mellitic Acid and the Constitution of Benzene.

The Terpenes.

The Peroxides and the Basic Properties of Oxygen.

On these subjects and a few other miscellaneous subjects, 278 papers were written.

A considerable proportion of the first volume is devoted to the indigo group and to the history of indigo synthesis. Baeyer's work on indigo and kindred subjects extended over a number of years and is perhaps the best known on account of its practical nature. As a direct result of his work, artificial indigo has been made commercially since 1891, and it was finally placed on the market at reduced prices in 1897.

His first work on this group began with the study of isatine, which he says was suggested from his work on the uric acid group,

"Meine Arbeiten über das Isatine sind ursprünglich von der Harnsäure Untersuchung ausgegangen." In perhaps none of his other works, unless it was in his study of the constitution of benzene, was there such a determination shown as in his indigo synthesis. He was not satisfied with the isatine and the nitropropionic acid syntheses, but continued the work with unabated zeal until not only a number of other important synthetic methods were discovered but also the structural formula of indigo.

Several hundred pages are devoted to his work on mellitic acid and to the constitution of benzene. This work, although perhaps not so fruitful as his indigo work, has nevertheless had an important bearing upon the benzene compounds. His identification of mellitic acid obtained from honey stone as benzene hexacarboxylic acid and its final "Abbau" into benzene, ranks in importance with the Wohl hydroxylamine reaction in the sugar group.

His work on the terpenes has likewise been of great significance. His system of naming the terpenes, his "Ortsbestimmung" and his synthesis from methylisopropylsuccinic ester has been of the greatest importance in the study of the terpene compounds.

His last work on the peroxides and the basic properties of oxygen is of the greatest importance. Three papers published in 1901 with Victor Villiger on the basic properties of oxygen following the important work of Collie and Tickle on the salts of dimethylpyrone and the quadrivalence of oxygen, have attracted the attention of chemists everywhere. In these papers, Collie and Tickle's work is expanded so as to cover the ethers, ethylene oxide and its related compounds, the alcohols, the acids, the esters, the aldehydes and the ketones, incidentally proving that the oxonium salts are formed with all carbon compounds containing oxygen except the peroxides.

Considerable space is given in the second volume to his work on dibenzalacetone and triphenylmethane. In these papers he has discussed the color theory, the structure and valence in triphenylmethane.

Baeyer is a great teacher as well as a great investigator. His students seem to catch the spirit of investigation, and scores of men trained in his laboratory are carrying out lines of work begun while studying with him.

He has written no text-books and has given the science little theory as compared with the great amount of research work he has done. When asked for theory he answered with experiment. Theories change but the experimental work found on the pages of these volumes will stand the test of time.

G. B. FRANKFORTER.

A LABORATORY HANDBOOK FOR THE ANALYSIS OF MILK, BUTTER AND CHEESE. By JAMES RITTENHOUSE EVANS, B.S. 1905. 60 pp., 2d ed. Price, \$1.40.

The chief merit of the book is its form of presenting methods in distinct steps, an arrangement that is of advantage for one using the methods for the first time. The methods could in many cases have been given with greater fulness to advantage. The method given for estimating casein and albumin is quite out of date. A serious omission is the failure to describe the use of the Quevenne lactometer in determining solids and solids-not-fat in milk. It is doubtful if one could detect skim-milk or watered milk satisfactorily by following the meagre directions given.

L. L. VAN SLYKE.

AMERIKANISCHES HOCHSCHULWESEN: EINDRÜCKE UND BETRACHTUNGEN. VON DR. W. BÖTTGER, Privatdozent an der Universität Leipzig. Leipzig: Wilhelm Engelmann. 1906.

The author of this little brochure spent a year in research work at the Massachusetts Institute of Technology and his impressions of the contrast between American and German universities are based upon careful observation and are extremely interesting and instructive. Their value is increased, especially for German readers, by means of a number of careful, detailed illustrations of the character of the work in American institutions.

W. A. N.

## RECENT PUBLICATIONS.

THE LABORATORY BOOK OF MINERAL OIL-TESTING. By J. A. Hicks. London: 1906. 88 pp. 2/6.

GUIDE PRATIQUE DE L'EXPERT-CHIMISTE EN DENREES ALIMENTAIRES. By D. Pellerin. Paris: Berger-Levrault. 1906. 8+682 pp. 11 francs.

CHEMIE UND CHEMISCHE WARENKUNDE F. ZOLLBEAMTE. UNTER BERÜCKSICHT DER ERLÄUTERGN. ZUM ZOLLTARIF F. DAS OSTER-UNGAR. ZOLLGEBIET VOM 13. By Franz Freyer. Wien: Firck. 1907. 8+562 pp. 6 marks.

REPETITORIUM DER CHEMIE MIT BESOND. BERÜCKSICHT DER F. DIE MEDIZINWISST. Ed. 12. Hamburg: Voss. 1906. 72+688 pp. 7 marks.

DIE VERSCHIEDENEN APPRETURVERFAHREN DER STREICHGARN-, KAMMGARN- U. CHEVIOTSTOFFE U. DER HALBWOLLENEN WAREN. By W. Jansen. Leipzig: "Spinner u. Weber" Hausdorff. 1906. 12+285 pp. 5 marks.

DIE GRENZEN DES PERIODISCHEN SYSTEMS DER CHEMISCHEN, ELEMENTE. By S. M. Losanitsch. Leipzig: Fock. 1906. 30 pp. 1 mark.

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